PROCESS DEVELOPMENT IN THE HYDROCARBON SYNTHESIS TO 1941

BY S. KODAMA, W. FUNABASHI, G. HASHIMOTO, T. HIRAO,
H. TAHARA, A. MATSUMURA, J. KATO, AND Y. TARAMA
(REVISED AND EDITED BY ROBERT C. GRASS)

* * * * * * * * * **Information Circular 7593**

UNITED STATES DEPARTMENT OF THE INTERIOR
Oscar L. Chapman, Secretary
BUREAU OF MINES
James Boyd, Director

Work on manuscript completed November 1950. The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is made: "Reprinted from Bureau of Mines Information Circular 7593."

Translation By Technical Japanese Translation Service, 1108 Morton Ave., Pasadena 13, Calif.

February 1951

PROCESS DEVELOPMENT IN THE HYDROCARBON SYNTHESIS TO 1941

by

S. Kodama,[1] W. Funabashi,[1] G. Hashimoto,[1]
T. Hirao,[1] H. Tahara,[1] A. Matsumura,[1]
J. Kato,[1] and Y. Tarama[1]

(Revised and Edited by Robert C. Grass[2])

CONTENTS

Page
Preface.. 1
Abstract... 2
Acknowledgments.. 2
Introduction... 3
Important aspects of plant design........................ 4
Inner-catalyst converter (100 l./hr.) using oil as a coolant... 6
    Description of equipment............................. 6
    Catalyst... 7
    Synthesis operation.................................. 7
Inner-catalyst converter (10 m.^{3}/hr.) using oil as coolant 8
    Description of equipment............................. 9
    Synthesis operation.................................. 10
Outer-catalyst converters using oil as coolant........... 10
    Converter with 3 m.^{3}/hr. throughput................... 10
        Description of equipment......................... 10
        Synthesis operation.............................. 11
    Converter with 10 m.^{3}/hr. throughput.................. 11
        Description of equipment......................... 11

---

[1] Kyoto Imperial University, Japan.
[2] Research chemist, Research and Development Branch, Office of Synthetic Liquid Fuels, Bureau of Mines, Bruceton, Pa.

Information Circular 7593

CONTENTS (Continued)

Page
Outer-catalyst converters using water as coolant.......... 12
  Converter with 6 m.^{3}/hr. throughput.................. 12
    Description of equipment.......................... 12
    Synthesis operation............................... 14
  Converter with 100 m.^{3}/hr. throughput................ 14
    Description of equipment.......................... 14
  Experimental procedure, cobalt catalyst............... 14
    Synthesis-gas preparation......................... 14
      Production of components, CO and H_2........ 14
      Purification and formulation of synthesis gas..................................... 16
    Catalyst.. 17
    Synthesis operation............................... 18
  Discussion of results................................. 19
  Experimental procedure; iron catalyst................. 27
    Synthesis-gas preparation......................... 27
      Production of components, CO and H_2........ 27
    Catalyst.. 30
    Synthesis operation............................... 31
  Discussion of results................................. 36
Calculation of heat-transfer data....................... 38
Summary... 40

ILLUSTRATIONS

Fig. — Follows page
1. Flow diagram (100 l./hr. inner-catalyst converter). 6
2. 25-mm. I.D. inner-catalyst converter............... 6
3. 35.7-mm. I.D. inner-catalyst converter............. 6
4. 55-mm. I.D. inner-catalyst converter............... 6
5. Flow diagram (10 m.^{3}/hr. inner-catalyst converter). 8
6. Organic-sulfur remover (10 m.^{3}/hr. inner-catalyst converter)................................. 8
7. 10 m.^{3}/hr. inner-catalyst converter................ 8
8. Detailed construction of figure 7................. 8
9. Equipment on downstream side of 10 m.^{3}/hr. inner-catalyst converter.......................... 8
10. Lamont boiler..................................... 8
11. 3 m.^{3}/hr. outer-catalyst converter................. 10
12. 10 m.^{3}/hr. outer-catalyst converter................ 10
13. Proposed outer-catalyst converter (tube centers 58 mm. x 51 mm.)...................................... 12
14. Proposed outer-catalyst converter (tube centers 43 mm. x 37.5 mm.).................................... 12
15. Hot-water circulation apparatus (6 m.^{3}/hr. outer-catalyst converter).............................. 12

ILLUSTRATIONS (Continued)

Fig.		Follows page
16.	Hot-water drum (6 m.^{3}/hr. outer-catalyst converter)	12
17.	6 m.^{3}/hr. outer-catalyst converter.................	12
18.	Detail of water-coolant pipe bends.................	12
19.	Hot-water drum, hot-water circulating pump, and 6 m.^{3}/hr. outer-catalyst converter.................	12
20.	General view of 100 m.^{3}/hr. pilot plant............	12
21.	100 m.^{3}/hr. outer-catalyst converter (original design)...	14
22.	100 m.^{3}/hr. outer-catalyst converter (as constructed)...	14
23.	Flow diagram of pilot-plant process................	14
24.	Gas-meter assembly: (left to right) H_2, water gas, synthesis gas, exit gas, gasol..................	14
25.	Wet-type gas desulfurizer: left, washing tower; right, tower for reactivating desulfurizing solution...	14
26.	Apparatus for removing organic sulfur..............	16
27.	Diagram of sulfur-removal system...................	16
28.	Temperature distribution in sulfur-removal furnace.	16
29.	Instrument panel...................................	18
30.	Water-cooled reactors: foreground, 6 m.^{3}/hr. unit; background, 100 m.^{3}/hr. unit.....................	18
31.	Heat exchangers: left, Diesel-oil cooler; right, gasoline cooler.................................	18
32.	Foreground, Diesel-oil separators; background, activated-carbon tower for adsorbing light oil...	18
33.	Thermocouple locations in 100 m.^{3}/hr. converter....	20
34.	Operating data for experiment 18...................	30
35.	Yield data for experiment 18.......................	30
36.	Co and Fe catalysts; experimental results..........	36
37.	Proposed flow diagram for recirculating tail gas...	38

PREFACE

In the summer of 1945, when it was evident that invasion of the Japanese home islands was imminent, the U. S. Naval Technical Mission to Japan was established to evaluate the accomplishments of the Japanese in naval technology and related fields. Of primary importance to the object of the mission was the acquisition of the maximum amount of information in the shortest possible time after the country was entered. Each day's delay allowed additional Japanese equipment and documents to be destroyed and made it easier for key Japanese personnel to disappear. With this in mind, the first entry into Japan by mission personnel was made early in September, and the activities of the mission were highly concentrated over the next few months, terminating finally in December.

One of the many phases of the Japanese technical war effort in which mission investigators were interested was the program directed toward obtaining liquid fuels from coal and other sources. The Japanese navy attached tremendous importance to research in this direction, and in 1945, approximately 3,200 persons, including about 400 technically trained personnel, were employed at the First Naval Fuel Depot at Ofuna, where every known phase of fuel and lubricant technology was being investigated. Research and development work involving both direct and indirect coal-hydrogenation processes also was being carried out in such places as the Institute of Fuel Technology at the Imperial University of Kyoto, the Imperial Fuel Research Institute of the Department of Commerce and Industry, the Hokkaido Synthetic Petroleum Co., Inc., and the Tokyo Institute of Physical Chemical Research. The relation of the Imperial Fuel Research Institute to the Japanese economy corresponds rather closely to that of the Bureau of Mines in the United States. In coal-hydrogenation investigations conducted there, emphasis was placed upon assays and fundamental studies rather than production. It was said that over a hundred Japanese coals had been so studied.

As Japan is extremely deficient in petroleum resources, it is not surprising to discover that organized effort had been made to obtain liquid fuels from sources that would otherwise appear fantastic. In attempts to supplement their supplies of motor fuel, so necessary to the prosecution of mechanized warfare, the Japanese investigated the potentialities of such source materials as orange peels, rubber, and pine needles and studied the hydrogenation of coal more extensively than any other nation except Germany. Their rewards for these efforts, however, were meager. Although plants for producing synthetic liquid fuels were constructed and operated, their output fell disastrously short of the magnitude necessary to support the Japanese military machine. Maximum production was attained in 1944, for which the total yearly synthetic-fuel output was reported as 955,000 barrels, divided among the various processes in the following manner: hydrogenation (of tars and other oils) = 5,780 barrels; Fischer-Tropsch process = 149,250 barrels; and low-temperature carbonization = 899,970 barrels.

To provide an insight into Japanese research methods and to determine the direction taken by synthetic fuel research in Japan both before and during World War II, mission investigators obtained a number of papers and reports from the organizations listed above. These papers, of which the following is exemplary, have been translated and carefully examined. For many reasons, the English translations must be regarded with reservations. The conversion of Japanese text to its English equivalent is complicated by extreme language difficulties; in many cases, words do not exist in the one language for ideas expressed in the other. The task was complicated further by a lack of familiarity with the field of synthetic liquid fuels on the part of some of the translators. In addition, it must be emphasized that many of the discussions to be found in these papers were based on theories which, at that time, were accepted as valid by most of the scientific world, but which have since been discarded in the light of subsequent experimental evidence. Despite the accompanying qualifications, it is felt that these papers are instrumental in establishing an appreciation of Japanese research efforts in the field of synthetic liquid fuels.

ABSTRACT

Starting on a small scale, the equipment for processing synthesis gas to form liquid hydrocarbons was expanded to handle 100 $m.^3/hr$. This reactor was successfully designed and constructed, and a basis for future design methods was established. Because, however, this work was carried out on an empirical basis, it is felt that a more thorough theoretical study should be made in an effort to increase the efficiency of the process, particularly in the development of a simpler converter.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the following contributions to this work: Y. Murata for catalyst preparation; W. Funazaka for water-gas production; Y. Iwasa and H. Shiraishi for hydrogen production; N. Mutsuda for gas purification; S. Matsummura, T. Umemura, Y. Takezoki, H. Tawara, K. Tarama, Y. Uo, K. Iwamoto, J. Kiomizu, and N. Mizutani for experimental work.

Financial and technical assistance was received from the main office of the Sumitomo Co., Ltd., the Sumitomo Chemical Engineering Corp., the Sumitomo Mining Corp., and Chemical Industries, Ltd. The authors are especially indebted to Y. Tsugami and Y. Yagi for particularly valuable technical help.

For the construction of the water-cooled converter, thanks are given to the Kawasaki Heavy Equipment Manufacturing Co. Technical advice was supplied by K. Gota and S. Tanaka.

For continual assistance and encouragement toward construction of the 100-$m.^3/hr$. converter, sincere thanks are due Professor Matsunaga of Osaka Imperial University.

We also acknowledge the assistance rendered by the following: S. Tsuneoka (Teikoku Fuel Co.); S. Nakai, T. Kamano, M. Takayama, Y. Tashiro, M. Zenko,

Original from THE OHIO STATE UNIVERSITY

M. Nakagawa, and G. Komori (Hokkaido Synthetic Fuel Co.); K. Horikawa, M. Umemura, S. Santo, and M. Takeda (Manchurian Synthetic Fuel Co.); M. Fukuda (student at the University of Kyoto); and to K. Kasai, G. Makai, K. Ichikawa, T. Mitsui, M. Nakayama, Y. Nishibayashi, Y. Takegami, and T. Yano (Fuel Chemistry Section, University of Kyoto). The operations were also assisted by the Army Fuel Institute and the Imperial Fuel Enterprisers Corp. Much credit is due to Professor Kita Gen-itsu for the planning stage.

INTRODUCTION

It is well known that the development of a new reaction on a laboratory scale does not by any means guarantee its successful application in an industrial-scale operation. As a matter of fact, the history of industrial chemistry contains numerous examples of where much more time and effort were consumed in developing a certain reaction to a commercial scale than were consumed in its discovery. The difficulties encountered in accomplishing this transition usually fall into two general classes, namely, (1) the selection of a suitable construction material to withstand the corrosive effects of the substances to be used in the process, and (2) the design and fabrication of suitable equipment to carry out the particular reaction on a commercial scale. These problems generally can be solved by constructing an experimental pilot plant where such chemical and mechanical difficulties can be anticipated and where important design data can be obtained.

Fortunately, in the synthesis of hydrocarbons no great problem exists in the choice of materials, but the design of the equipment presents many difficulties. The design of equipment for the chemical process industry constitutes one of the most important departments in the science of chemical engineering. This branch of science, however, has not developed as yet to a level where such design may be achieved successfully solely by the use of pencil and paper. One reason for this may be the inadequacy of the actual theories on which the science of chemical engineering is currently based. However, it seems probable that incomplete knowledge of the actual values for constants, such as the heat conductivity and elasticity of construction materials, has been a greater obstacle.

In conducting the pilot-plant experiments on the hydrocarbon synthesis at Kyoto Imperial University, a 5-year program was planned to culminate in operations on a scale representative of that of an actual industrial plant. This size was thought to be a pilot plant one-tenth the size of that to be used industrially, or one that would handle 100 $m.^3/hr.$ of gas. The objectives of the experimental program were proposed as follows:

1. To use as many theoretical calculations as possible in the design of the pilot plant.

2. To derive the most accurate figures possible by laboratory methods for all experimental data, even if they appear to be of dubious value.

3. To enlarge gradually the scale of the equipment employed to approach commercial-scale operation.

In the opinion of the author, the above criteria should be applied to all pilot-plant experiments. Much time, labor, and money have been wasted in Japan on pilot-plant experiments because such a program was not followed. Of course, depending on the time and money available and, perhaps, on the knowledge of the scientists involved, rigid adherence to such a pattern may not be possible. It is believed, however, that the success of the program at Kyoto, which was completed in 3-1/2 years instead of the anticipated 5, was strongly dependent on this program. In the final expansion of the equipment to a throughput of 100 $m.^3$/hr., it was not even necessary to make a preliminary test of the equipment. Actual operations were conducted immediately after construction was completed; continuous operations were carried out for 2 weeks with no significant difficulty at any time.

Since 1927, extensive studies have been conducted on catalysts for the synthesis of petroleum hydrocarbons from carbon monoxide and hydrogen. (Fischer-Tropsch process) in the laboratories of Professor Kita of Kyoto Imperial University. Among the successful catalysts discovered was one containing iron as the main constituent. Bench-scale studies of the Fischer-Tropsch synthesis made with cobalt catalysts were begun in 1939 in a water-cooled reactor at a throughput of 6 cubic meters of synthesis gas per hour. The successful completion of these studies in the fall of 1939 led to a contract for the design and construction of a pilot plant to accomodate a synthesis-gas throughput of 100 cubic meters per hour, the work to be completed by July 1940. On July 17, 1940, experimental operations were begun in this pilot plant. A continuous operation, experiment No. 17, was started on August 3 and continued for 18 days; a detailed description of the experiment is given in this report. On the basis of these results, the Hokkaido Synthetic Fuel Co., Ltd., proposed the design and construction of a commercial-scale plant to accomodate a throughput of 1,000 cubic meters of synthesis gas per hour. Because of the acute shortage of cobalt, however, these plans, which called for the use of cobalt catalysts, were temporarily abandoned, and intensive research on iron catalysts was begun in the 100 $m.^3$/hr. converter.

Extensive studies of iron catalysts at the Kita laboratory showed that 151 cc. of liquid products could be obtained from 1 cubic meter of a 1-to-1 mixture of CO and H_2, a yield that compared favorably with cobalt catalysts. Although a short life was anticipated for iron catalysts, laboratory tests demonstrated that it was possible to extend the effective life considerably in several ways, among them by lowering the reaction temperature and by using a hydrogen-rich synthesis gas. Enough iron catalyst was prepared, therefore, to allow operation on a pilot-plant scale. The experiment covering this work (No. 18) extended from October 17 to November 6, 1940, and the actual life of the catalyst was found to be even greater than that predicted by laboratory tests.

IMPORTANT ASPECTS OF PLANT DESIGN

The equipment comprising the pilot plant for the synthesis of hydrocarbons consists of many units, such as the desulfurizer, the converter, the condenser, the activated charcoal absorber, and others, but the most important, and the most difficult in its design, is the converter in which the catalytic reactions take place. The greater part of the following discussion is devoted, therefore, to the converter.

Original from THE OHIO STATE UNIVERSITY

The difficulty in designing a suitable converter lies in the fact that the reactions occurring in the synthesis of hydrocarbons are chiefly heat-producing and that the temperature of the catalyst bed as a whole must be maintained at a constant value with little or no fluctuation. According to calculations made in this laboratory, the heat produced by the hydrocarbon synthesis using 1 cubic meter of gas containing pure carbon monoxide and hydrogen[3] reaches 450 kcal. If the reaction is conducted adiabatically, the catalyst bed may reach temperatures over 1,000° C. This obviously cannot be tolerated, as the catalysts found to be effective in the synthesis of hydrocarbons have proved to be extremely sensitive to temperature; a variation of more than 2° C. in the catalyst temperature produced undesirable results. Thus, for each catalyst used in the hydrocarbon synthesis, there exists an optimum temperature. A slight decrease in this temperature will cause an immediate decrease in the reaction velocity with the formation of smaller amounts of hydrocarbons; similarly, a slight increase in this optimum temperature will tend to produce a large amount of methane and other gaseous hydrocarbons, with the result that less liquid products are formed. Therefore, in the design of a converter, it is of utmost importance to arrange to remove the heat of reaction and to maintain the catalyst bed within the required temperature limits. Eventually this problem can be reduced to one of heat transfer.

The basic relationship for the transfer of heat is well known. If the cooling surface area is represented by "A" and the heat transfer coefficient is "K" when the average temperature difference is "Δt," then the amount of heat that will flow in a unit of time will be:

$$q = K A \Delta t.$$

Where a simple wall separates the cooling medium from the heat source, the heat-transfer coefficient, K, may be defined as:

$$\frac{1}{K} = \frac{1}{h_a} + \frac{\delta}{\lambda} + \frac{1}{h_b}$$

where h_a is the film coefficient on the side of the wall containing the heat source (in this case, a gas), and where h_b is the film coefficient on the side of the wall containing the cooling (liquid) medium; δ represents the thickness of the separating wall, and λ is its thermal conductivity.

Studies by such investigators as A. P. Colburn[4] on the film coefficient existing when gas is passed through a tube filled with catalyst are very incomplete. This lack of fundamental information discourages any successful design of a converter by theoretical considerations alone. Either water or oil can be used as coolants, but because no method is known for computing the film coefficients for these substances when they are used in an apparatus of complicated shape, it was necessary to determine experimentally the area of cooling surface required per unit volume of catalyst. At first, synthesis was carried out in an apparatus into which 100 l. of gas was introduced per hour.

---

[3] To be published.

[4] Colburn, A. P., Ind. Eng. Chem., vol. 23, 1931, p. 910.

Original from THE OHIO STATE UNIVERSITY

From consideration of previous results, the experimental scale was gradually enlarged, and the type of coolant and the distribution of the cooling pipes were varied to obtain the data necessary for subsequent expansion. A detailed description of the converters studied follows; table 1 lists the types of converters investigated.

TABLE 1. - Types of converters investigated in pilot-plant synthesis of hydrocarbons by Fischer-Tropsch process

Hourly gas flow rate	Type of heat removal employed	Date testing completed
100 l.	Hot oil outside of catalyst tubes.	July 12, 1937
10 m.^{3}	do.	May 13, 1938
3 m.^{3}	Hot oil inside tubes, catalyst outside.	July 13, 1938
10 m.^{3}	do.	November 13, 1938
6 m.^{3}	Hot water inside tubes, catalyst outside.	September 14, 1939
100 m.^{3}	do.	July 15, 1940

INNER-CATALYST CONVERTER (100 l./HR.) USING OIL AS COOLANT

Description of Equipment

Three converters, each differing in catalyst-volume:cooling-area ratio, were constructed. Three tubes, possessing inside diameters of 25 mm., 35.7 mm., and 55 mm., were each filled with 100[5] cm.^{3} of catalyst. A gas flow of 100 l./hr. was then passed through each tube while hot oil was circulated around the tubes as a cooling medium.[6] The formation of product oil was then correlated with the temperature difference between the cooling medium and the catalyst.

The flow diagram of the process as it was carried out in this test is shown in figure 1. The synthesis gas used was first passed through a flow meter (1), where its volume was measured, following which it was passed through a dehydrator (2), where its water content was removed. The dried gas was then heated to approximately reaction temperature in a preheater (3), from which it was sent into the converter (4). The products and the unreacted gases were led to a cooler (5), where the oil fraction of comparatively high boiling point (Diesel oil) and the water were condensed and collected (6). The volatile oil product and the gaseous fractions such as propane and butane, which did not condense in the cooler, were then adsorbed in activated charcoal traps (7). The remaining gas was passed through the wet test meter (8) before it was released. A constant temperature was maintained in the converter in the following manner: The coolant oil stored in

---

[5] Editor's Note: This figure is given as 1,000 cm.^{3} in later paragraphs.

[6] Editor's note: Same as German "inner-catalyst converter." Refer to Bureau of Mines Inf. Circ. 7587, The Evaluation of Converters for Exothermic and Endothermic Catalytic Reactions Occurring within Narrow Temperature Limits, by Gustav Wirth, translated and revised by R. C. Grass and H. J. Kandiner.

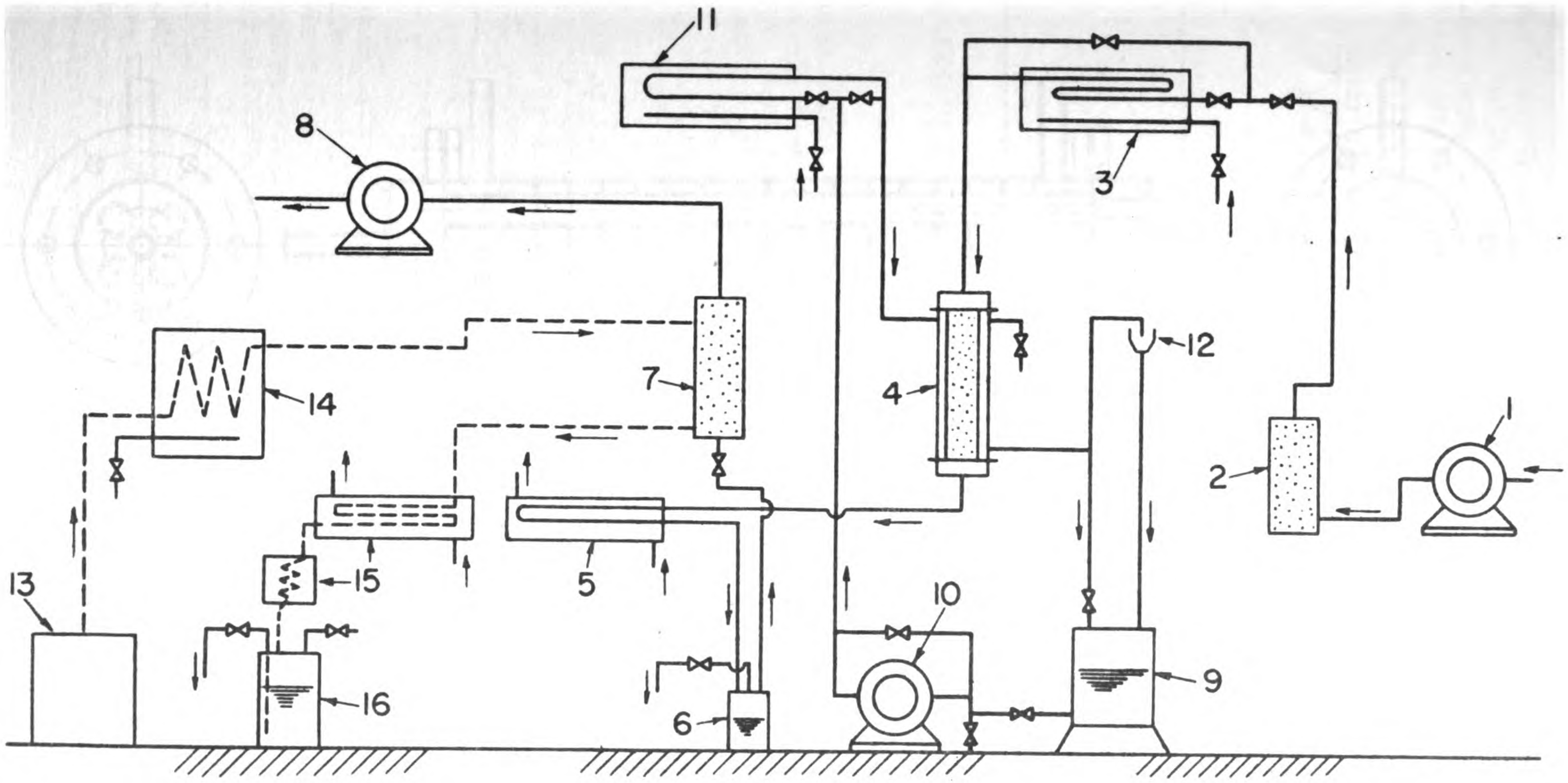


Figure 1. - Flow diagram (100 l./hr. inner-catalyst converter).

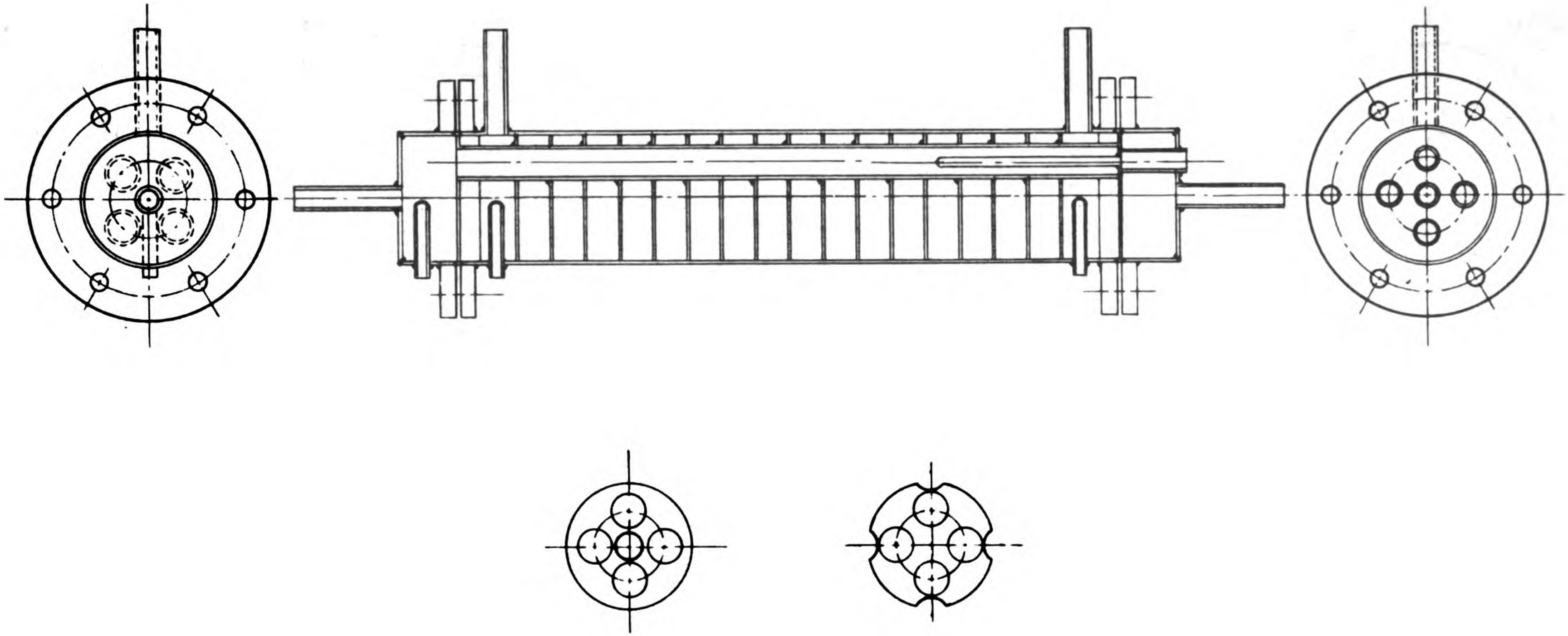


Figure 2. - 25-mm. I.D. inner-catalyst converter.

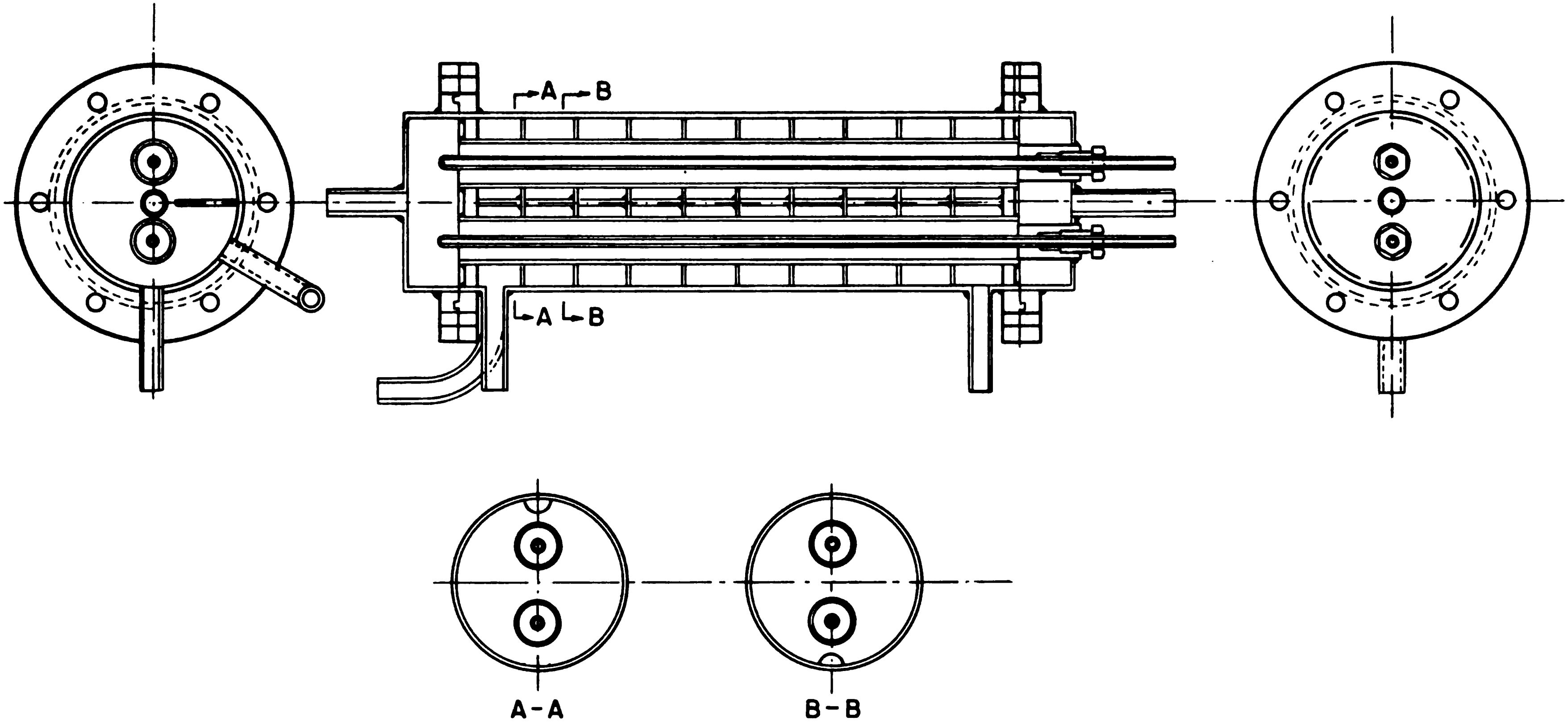


Figure 3. - 35.7-mm. I.D. inner-catalyst converter.

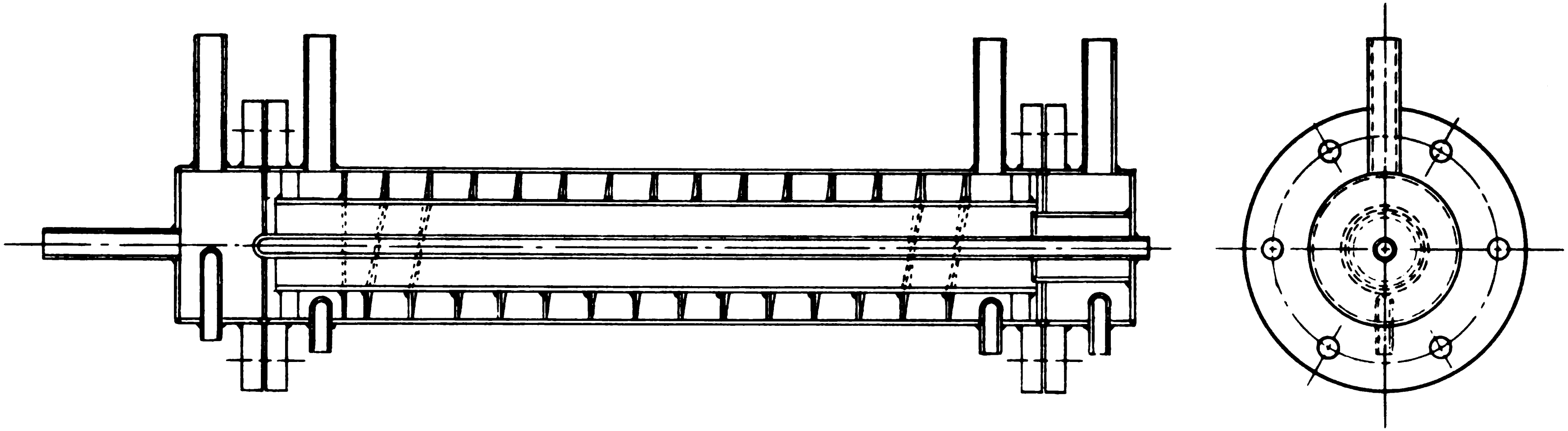


Figure 4. - 55-mm. I.D. inner-catalyst converter.

tank (9) was sent into a preheating apparatus (11) by pump (10). The oil, heated to the desired temperature, was then passed through the converter (4), after which it was collected in tank (12) and returned to the storage tank (9).

The volatile oil fraction adsorbed on the activated carbon was stripped off with superheated steam. Auxiliary equipment included the steam boiler (13), the steam superheater (14), the cooling equipment for the discharged volatile oil and steam (15), and the collecting tank (16).

Cross sections of the converters used in this test are illustrated in figures 2, 3, and 4, which show respectively, that four 25-mm I.D. catalyst tubes, two 35.7-mm. I.D. catalyst tubes, and one 55-mm I.D. catalyst tube were contained in the converters. In all three cases, approximately 1,000 cm.^{3} of catalyst was used. Special attention was devoted to obtaining the maximum possible velocity of the cooling oil and to eliminating dead spaces in the flow of cooling medium. Baffle plates were distributed throughout the converter to promote thorough mixing of the cooling medium and thus maintain a maximum thermal conductivity to the cooling oil.

Catalyst

The catalyst employed had the following composition: 100 Co: 12.5 Cu:2.5 Th:1.25 U:125 diatomaceous earth. In laboratory experiments using this catalyst,[7] an oil yield of 100 to 110 cm.^{3}/m.^{3} of synthesis gas was obtained. The cooling oil was held as near to 205° C. as possible. Synthesis gas composed of one part CO to two parts H_2 was used. The results of these tests are summarized in table 2.

TABLE 2. - Summary of results obtained with inner-catalyst converter using hot oil as a cooling medium

(Flow rate of $2H_2$:1CO gas = 100 l./hr.)

Inside diameter of catalyst tube, mm.	Maximum temperature difference between cooling medium and catalyst, $^\circ$C.		Oil yield, cm.^{3}/m.^{3}	Catalyst efficiency, cm.^{3}/m.^{3}
	At start	At standard conditions		
25	3	3	98	110
35.7	46	10	78	101
55	138	23	40	101

Synthesis Operation

After reduction of the catalyst in the 55-mm. I.D. catalyst tube, the temperature of the cooling oil was raised to nearly the proposed synthesis temperature of 205° C. On initiating a flow of synthesis gas, however, the temperature of the catalyst bed suddenly increased until, at 342.5° C., it was evident that maintenance of a constant temperature in the catalyst bed was impossible with this type of operation. Nevertheless, the synthesis was continued by lowering the temperature to which the cooling oil was preheated, thereby controlling the increase in temperature of the catalyst bed. Control was also facilitated as the catalyst became deactivated and evolved less and less heat of reaction, but, even after 30 hours of operation, a temperature difference of 23° C. was observed. The oil yield was only about 40 percent of that obtained in the laboratory, and it was concluded that, in a converter of these dimensions, the cooling surface was not sufficient to remove effectively the heat produced by the synthesis reactions.

---

[7] Kyoto Imperial University, Chemical Research Institute Lecture Series No. 8, 1938, p. 11.

Similar unfavorable results were obtained in the 35.7-mm. I.D. catalyst tubes. Although, by carefully controlling the preheating temperature of the cooling oil, it was possible to continue the operation, the product oil yield was inferior.

On the other hand, the results obtained with the 25-mm. I.D. catalyst tubes were very good. Throughout the operation, approximately 36 hours, the catalyst-coolant temperature difference remained within 3° C., and no difficulty was encountered in controlling the temperature of the catalyst bed. Furthermore, the product oil yield from a continuous 12-day period was superior to that obtained in the laboratory.8/ These results indicate that for effective removal of the heat of reaction in the hydrocarbon synthesis, a minimum cooling surface equivalent to that of a 25-mm. I.D. catalyst tube is necessary.

INNER-CATALYST CONVERTER (10 m.^{3}/hr.) USING OIL AS COOLANT

The equipment used in this set-up was 100 times the capacity of that used in the previous experiments. It was constructed and operated for the following reasons:

(a) Up to this time, synthesis gas composed only of pure hydrogen and pure carbon monoxide, prepared from formic acid, was used. Progression to larger quantities of feed gas required the use of water gas made from coke. It therefore became necessary to construct an apparatus to remove undesirable feed-gas contaminants such as hydrogen sulfide and organic sulfides.

(b) Although, from the previous orienting experiment, a cooling surface equivalent to the 25-mm. I.D. catalyst tube was indicated to be sufficient, the short length of the catalyst tube (500 mm.) precluded any definite decisions. It was observed that, compared to the amount of heat carried off by the cooling oil through the walls of the catalyst tube, a great amount of heat also was carried away through the upper and lower parts of the catalyst tube, and this assisted considerably in cooling the catalyst bed. It was necessary, therefore, to determine whether a cooling surface equivalent to a 25-mm. I.D. tube would continue to be sufficient when the catalyst bed length was increased beyond 500 mm.

8/ See footnote 4.

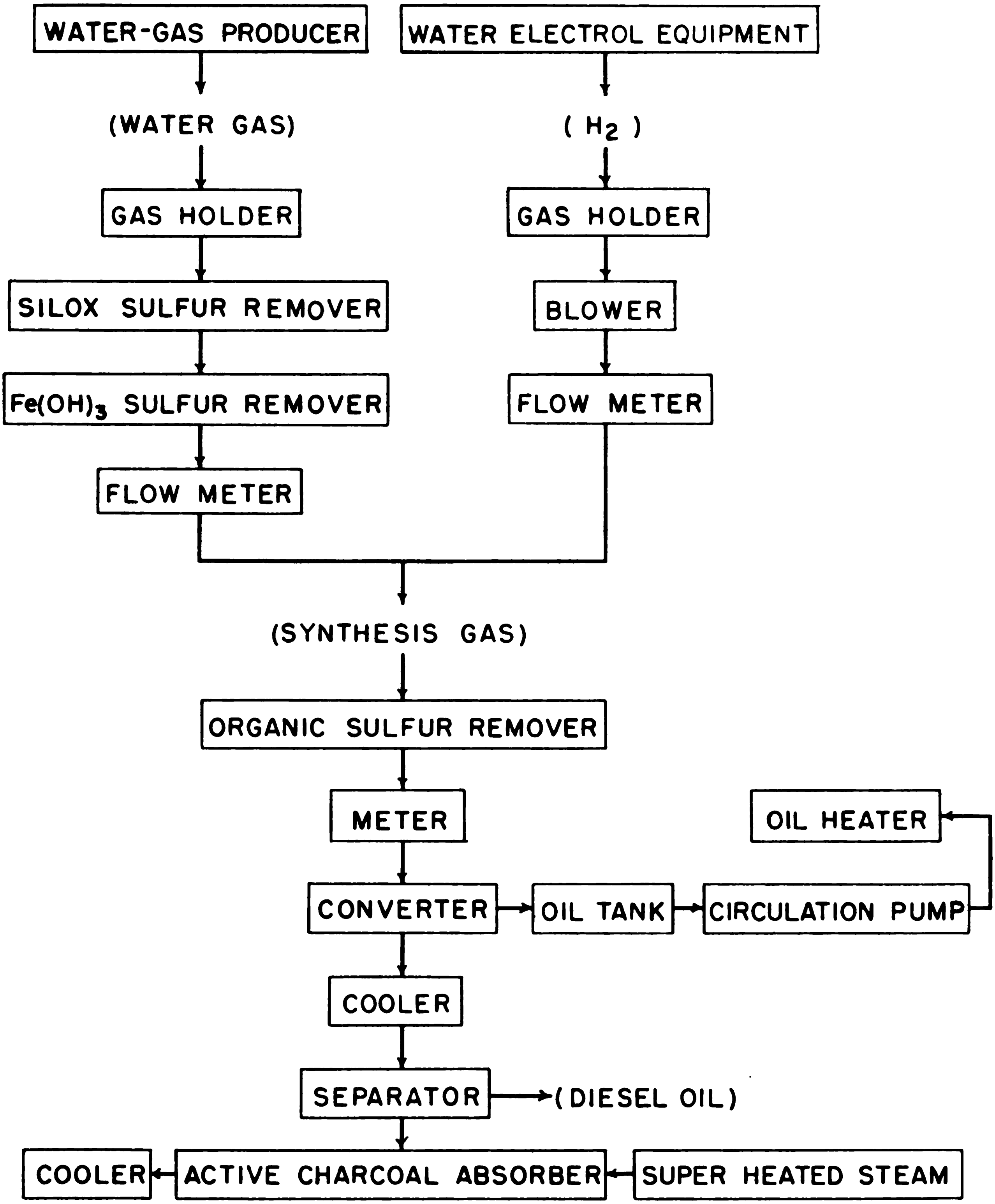


Figure 5. - Flow diagram (10 m.^{3}/hr. inner-catalyst converter).

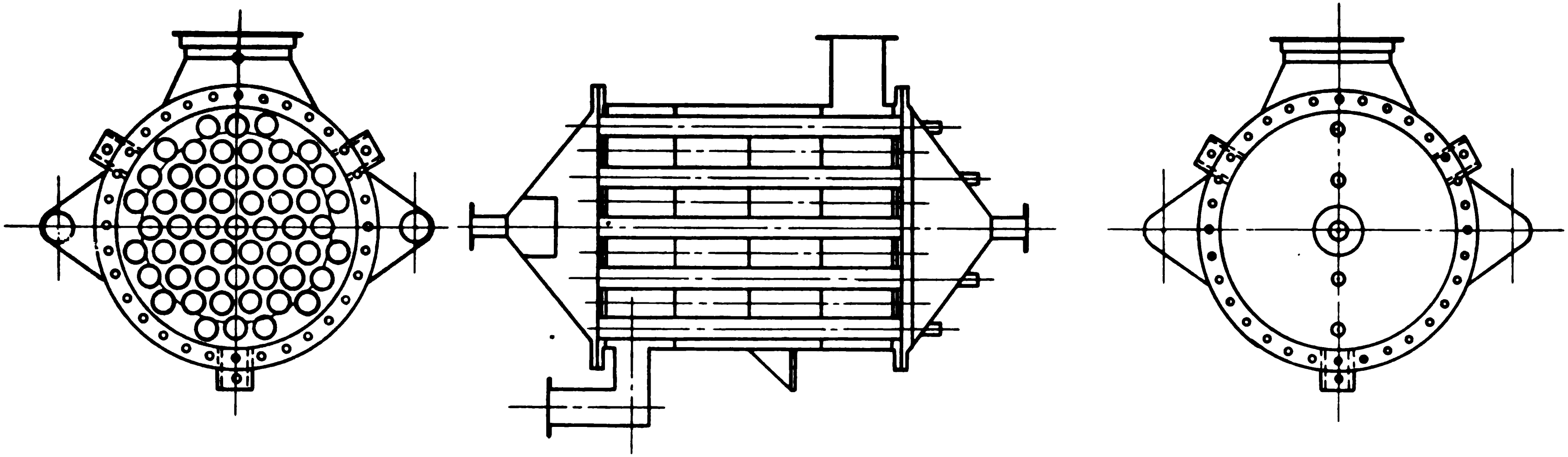


Figure 6. - Organic sulfur remover (10 m.^{3}/hr. inner-catalyst converter).

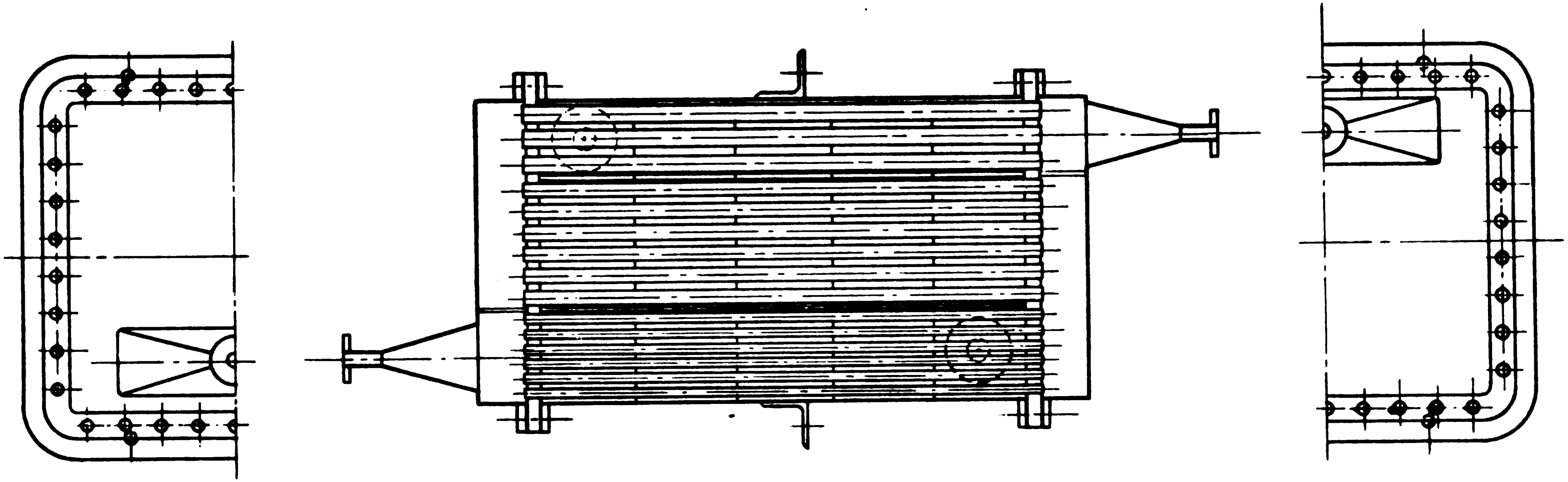


Figure 7. - 10 $m.^3$/hr. inner-catalyst converter.

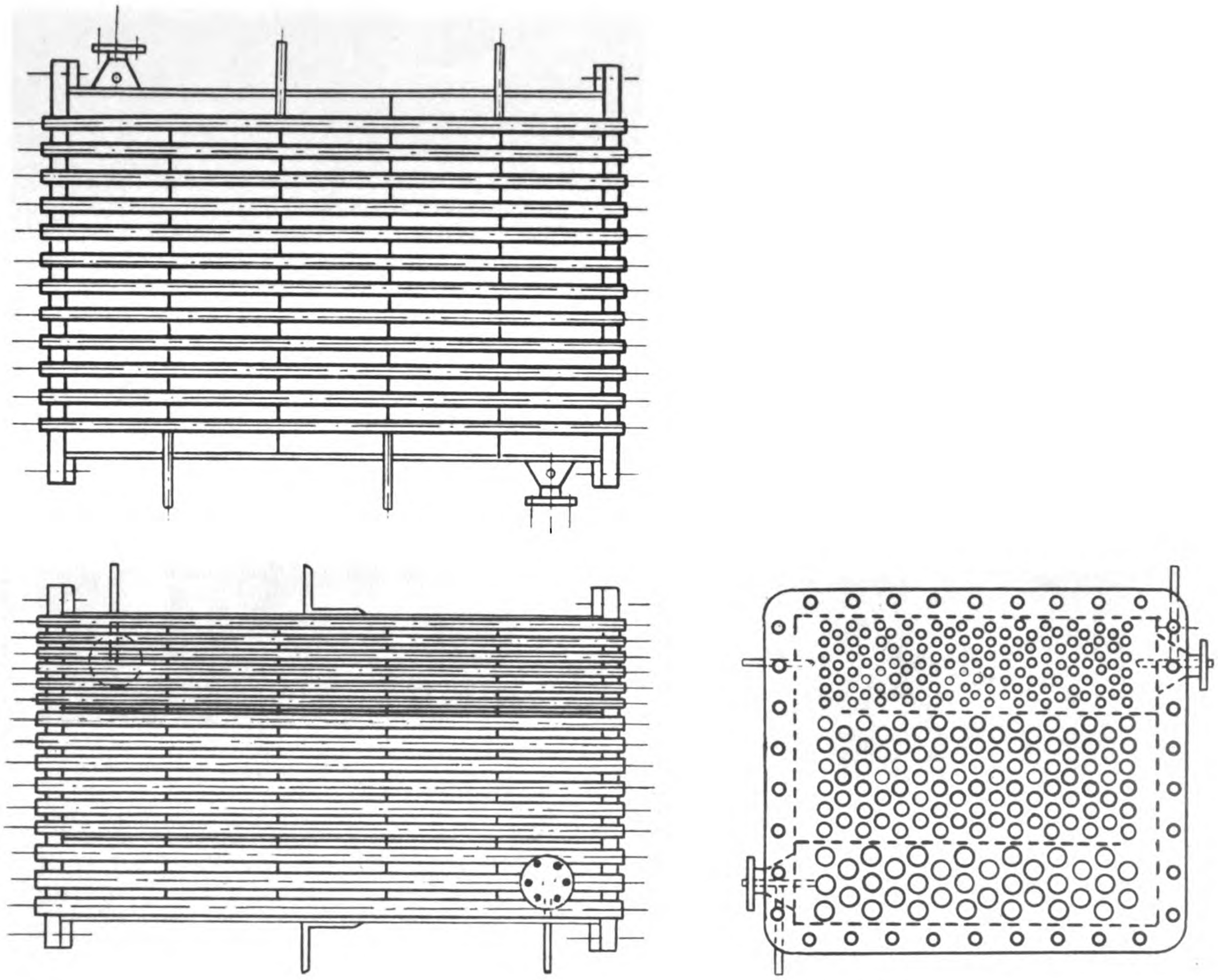


Figure 8. - Detailed construction of figure 7.

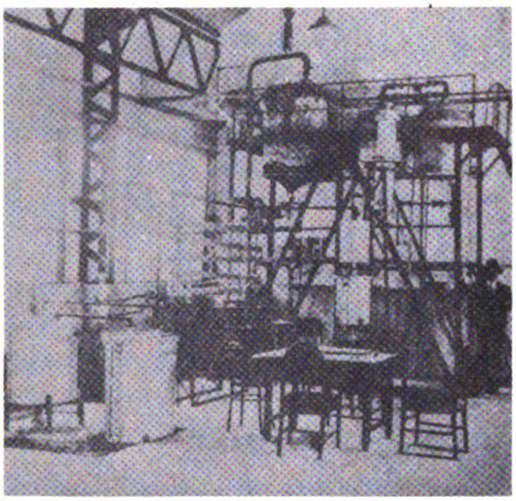


Figure 9. - Equipment located on down-stream side of 10 cubic meter per hour inner-catalyst converter.

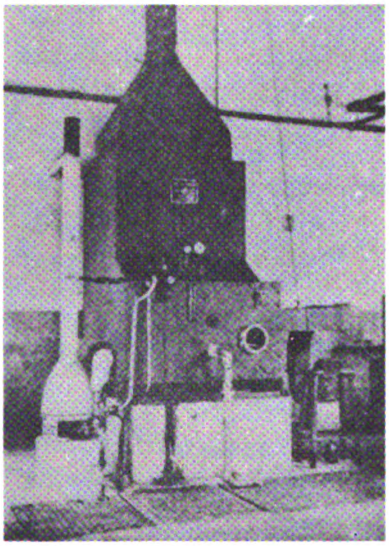


Figure 10. - Lamont boiler.

(c) Finally, in preparing for the eventual design and construction of commercial-scale equipment, it was necessary to design and build on a small scale (at least once) such units as the cooler and active charcoal absorber. The flow diagram for the synthesis of hydrocarbons in this unit is shown in figure 5.

Description of Equipment

The construction of the organic sulfur remover is shown in figure 6. In this particular experiment the gas was passed through a pipe filled with luxmasse and containing 10 percent each of NaOH and $Cu(OH)_2$ and heated externally to 200°-260° C. by gas firing. In industry, organic sulfur is usually removed by preheating the gas to 200°-250°C. and passing it over the purifying agent. External heating of the purifying agent, itself, is not common. Where low mass flows (such as 10 $m.^3$/hr.) are involved, however, the heat capacity of the system is so small that preheating cannot be relied upon to maintain the desired temperature. However, initial attempts to heat the raw gas by simply passing through an externally heated cylindrical container filled with the purifying agent were unsuccessful, because the heat conductivity of the granular purifying agent was very low, and uniform heating of the mass by external firing was extremely difficult. When heating was increased to raise the temperature of the inner portion of the granular materials, the outer sections of the granular mass became overheated, and a reaction was initiated that ultimately produced methane from CO and H_2. Moreover, this reaction, being exothermic, rapidly increased the temperature of the solid granules, once started, and created the problem of controlling this temperature rise and of cooling the agent to the desired temperature. For these reasons, the unit shown in figure 6 was designed to control the temperature of the purifying agent and maintain it uniform.

As shown in figures 7 and 8, the construction of the inner-catalyst converter with a throughput capacity of 10 $m.^3$/hr. is identical in principle to that of the unit of 100 l./hr. capacity; i.e., the catalyst is contained inside the tubes, whereas the outside of the tubes is cooled with oil. This converter was constructed with three banks of tubes, consisting of 127 tubes of 5/8-inch I.D. (approximately 15 mm.); 94 tubes of 1-inch I.D. (25 mm.); and 35 tubes of 1-1/4-inch I.D. (31 mm.), respectively. The synthesis gas was passed through the unit in the direction of increasing tube diameter for the following reasons: (1) As the converter becomes larger, the cooling surface ratio provided by a 25-mm. I.D. tube arrangement might be insufficient; (2) the current synthesis theory[9] indicates a highly exothermic reaction near the entrance of the catalyst chamber, so that a large cooling surface at this point is desirable; and (3) by filling each bank independently, the effect of cooling surface could be studied. Baffle plates were used to increase the path traveled and the velocity of the cooling oil and to minimize dead space. Figure 9 is a photograph of the equipment on the downstream side of the converter.

9/ To be published.

Synthesis Operation

The 10-m. /hr. unit was completed toward the latter part of April 1938. Beginning May 2, a 12-day run was carried out, in which 100.1 of Co catalyst was used.[10] The results have been reported.[11] The maximum temperature difference in the apparatus was about 6° C., with an over-all average of less than 5°, showing that the cooling surface was sufficient for removal of the heat of reaction. As the result of tests in this converter, it was concluded that a cooling surface ratio equivalent to that obtained with a 25-mm. I.D. tube adequately removed the heat generated by the synthesis of hydrocarbons in a converter of this design.

OUTER-CATALYST CONVERTERS USING OIL AS COOLANT

From the above experiments it was obvious that a certain ratio of cooling surface to catalyst volume was necessary for practical operation of an inner-catalyst converter in the hydrocarbon synthesis using oil as coolant. However, the application of hot water as a coolant for catalyst beds seemed preferable to oil, as water was already in use industrially and possessed the advantage that as the heat of reaction was removed through vaporization of water a constant temperature was more easily maintained. Moreover, this utilization of reaction heat to produce steam was an additional economic advantage. As the reaction temperature was greater than 100° C., however, it was necessary to use water under pressure, which is undesirable in design and construction economics. In order to minimize the amount of pressurized construction, therefore, it was desirable to pass the coolant through the tubes instead of around them.[12] As a result, the fundamental problem in the design of the outer-catalyst converter was determination of the necessary spacing between the cooling tubes. An approximation could be obtained from the results of previous experiments, but, as the heat-transfer film coefficient of a gas varies according to whether the gas is flowing inside or outside of a tube, further experiments were indicated. Although the liquid film coefficient of heat transfer for water is much greater than that of oil and suggests that a distance between cooling tubes equal to that used in the previous converter would be too small, the gas film coefficient is probably the controlling factor. In order to obtain some orienting data preparatory to the use of water coolant, preliminary experiments were made in the following converters using oil as the cooling medium.

Converter With 3-m.^{3}/hr. Throughput

Description of Equipment

To obtain design data on these points, the converter shown in figure 11 was constructed with a catalyst capacity of 30 liters and a maximum throughput

---

[10] Editor's note: Presumably the same type used in the smaller unit.

[11] Kyoto Imperial University, Chemical Research Institute Lecture Series No. 9, 1939, p. 89.

[12] Editor's note: Same as German "outer-catalyst converter." Refer to Bureau of Mines Inf. Circ. 7587, The Evaluation of Converters for Exothermic and Endothermic Catalytic Reactions Occurring within Narrow Temperature Limits, by Gustav Wirth, translated and revised by R. C. Grass and H. J. Kandiner, Nov. 1950, 13 pp.

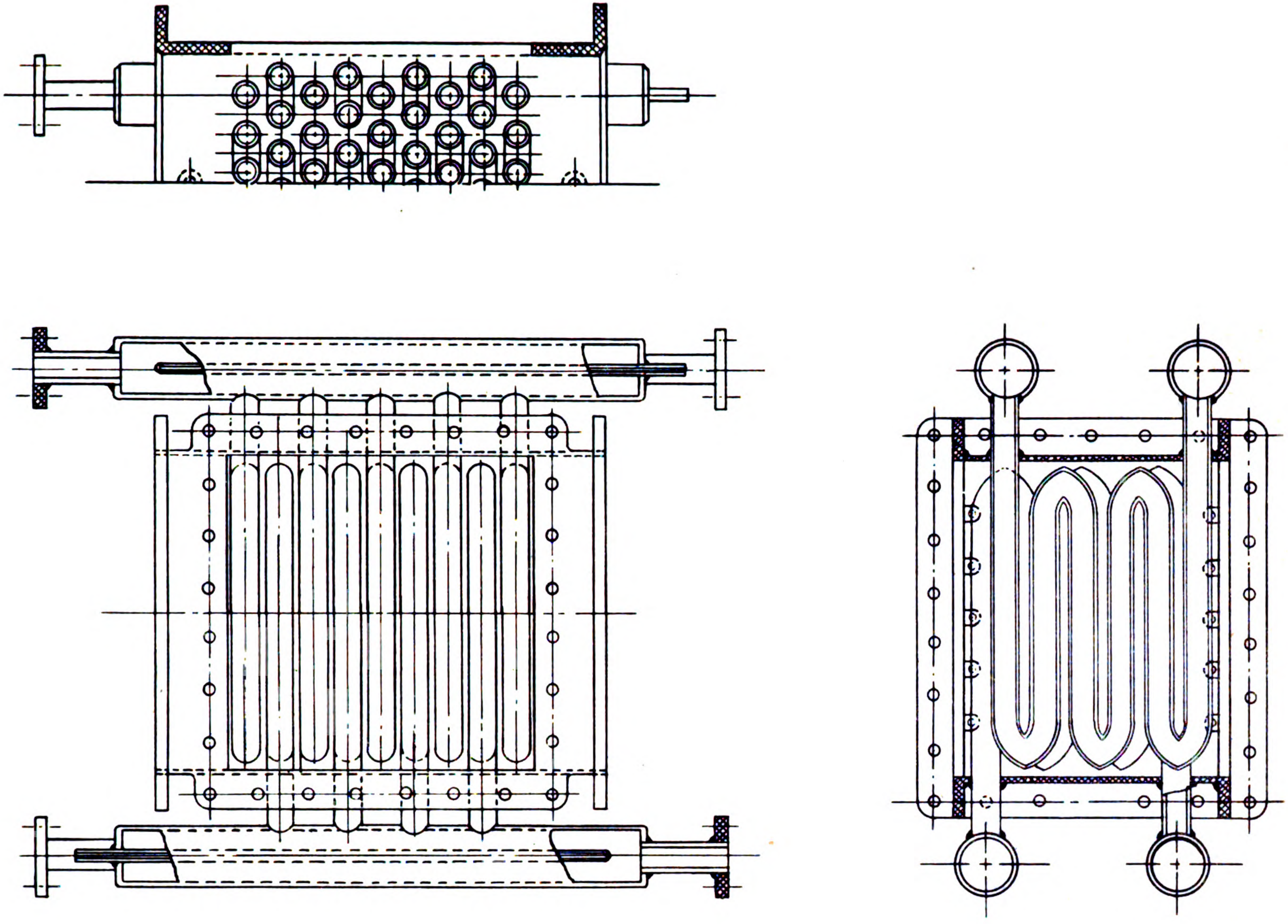


Figure 11. - 3 m.^{3}/hr. outer-catalyst converter.

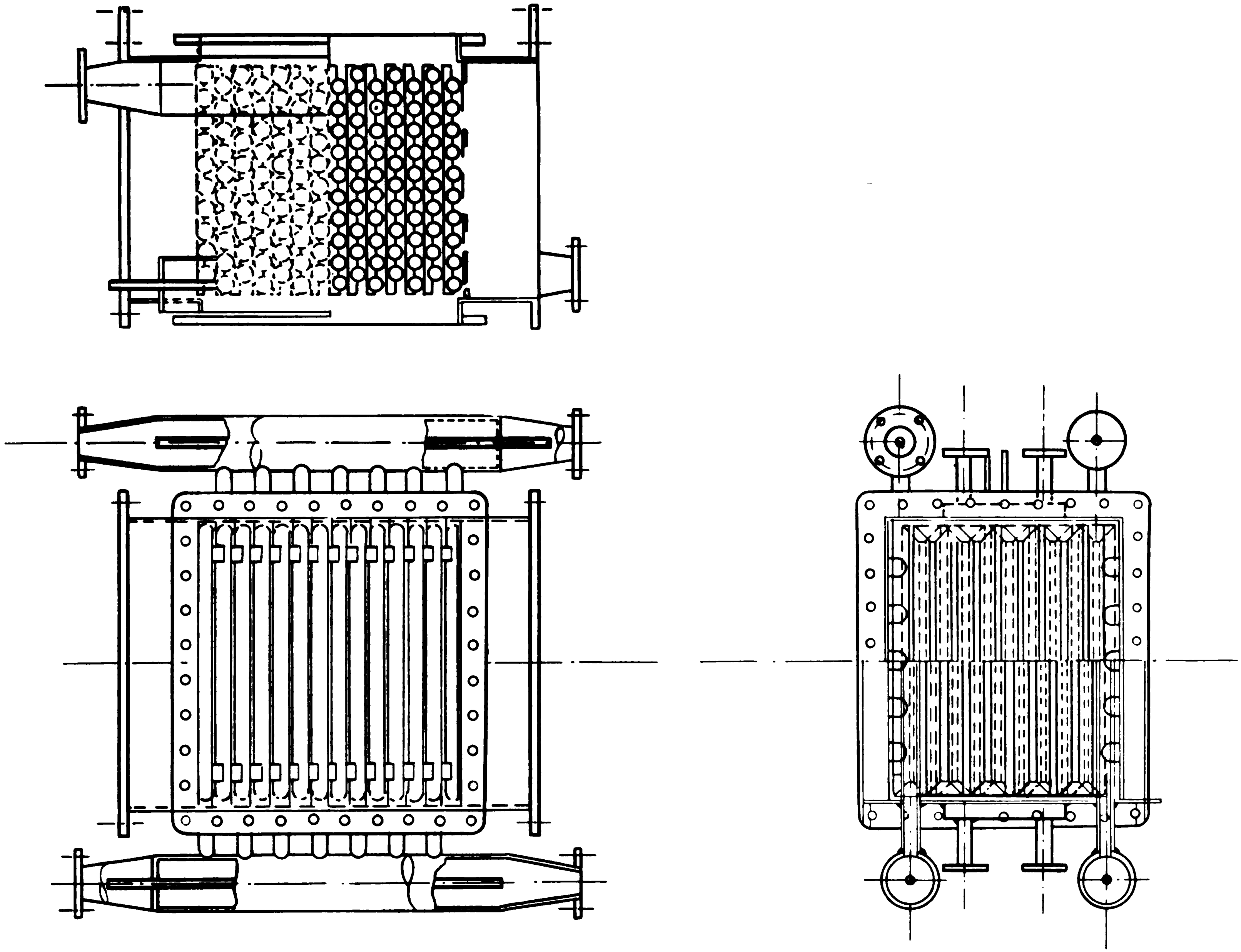


Figure 12. - 10 m.^{3}/hr. outer-catalyst converter.

of 3 m.^{3}/hr. The coolant from the manifold was separated into individual cooling tubes and, after passing through the reaction zone, was collected in a manifold, passed through a heat exchanger, and recirculated. The most difficult problem faced in the construction of this converter was that of providing a gas-tight seal at the junction of the coolant tube and reactor wall because of the small spacing between the tubes. In order to facilitate the welding employed to make this seal, the inlet and outlet lines were made interchangeable, and bends were made inside instead of outside of the catalyst space. In this converter, cooling tubes 34-mm. O.D. and 26.7-mm. I.D. were spaced 48 mm. vertically and 42 mm. horizontally (center-to-center), providing a cooling surface ratio somewhat less than that contained in the 35.7-mm. I.D. inner-catalyst converter. It was felt that a smaller cooling surface would be required in this design, because the flow of gas across the cooling tubes should increase the gas film coefficient.

Synthesis Operation

Operation of the converter was begun by using oil as a coolant and 30 liters of cobalt catalyst; the temperature distribution in the catalyst bed shown in table 3 was obtained. After 17 hours of operation, the section of catalyst at the gas inlet showed a marked increase in temperature, and the temperature difference between this section and the cooling oil reached 36° C. Temperature control of the catalyst bed was very difficult, indicating that the cooling surface was insufficient in this type of cooling tube arrangement. By packing the first half of the catalyst bed with a mixture of catalyst and inert material, temperature control of the whole bed was possible to a certain extent.

TABLE 3. - Distribution of temperature in catalyst bed during operation of oil-cooled outer-catalyst converter

(Throughput = 3 m.^{3}/hr.; 30 liters of cobalt catalyst)

Operating time, hours	Temperature cooling oil, °C.		Temperature catalyst bed, °C [a]			Gas flow, m.^{3}/hr.	Contraction, percent
	Inlet	Outlet	1	2	3		
5.........	211	211	213	206	207	2.8	45.6
17.........	204	204	240	200	200	3.4	43.3
29.........	210	210	221	216	210	3.3	49.5
41.........	211	210	213	216	213	4.3	36.8
53.........	220	220	223	225	221	2.9	45.7
65.........	215	215	215	216	217	3.0	39.0

[a] Locations numbered progressively further from converter inlet.

Converter With 10-m.^{3}/hr. Throughput

Description of Equipment

To increase the cooling surface:catalyst-volume ratio, another converter was constructed, as shown in figure 12, in which the spacing of the cooling tubes was smaller. As a large percentage of the heat generated in the

3-m.^{3}/hr. converter was lost through the converter walls, the maximum throughput of the new converter was increased to 10 m.^{3}/hr. and its capacity to 100 liters of catalyst. The same size cooling tubes were used spaced (center-to-center) at 45-mm. vertical intervals and 39-mm. horizontal intervals. Table 4 shows the temperature distribution existing in a bed containing 95 liters of a cobalt catalyst. A maximum temperature difference of 9° C. was maintained, and the temperature was relatively easy to control. This particular cooling surface ratio must therefore have been sufficient, even though it was less than that of the inner-catalyst converter.

TABLE 4. - Distribution of temperature in catalyst bed during operation of oil-cooled outer-catalyst converter

(Throughput = 10 m.^{3}/hr.; 100 liters of cobalt catalyst)

Operating time, hours	Temperature cooling oil, °C.		Temperature catalyst bed, °C.a/				Gas flow m.^{3}/hr.	Contraction, percent
	Inlet	Outlet	1	2	3	4		
25.......	210.5	210	210	217	215	216	9.0	39.7
33.......	211	211	213	219	216	211.5	8.5	42.3
41.......	210	210	210.5	218.5	214	214.5	9.7	43.7
49.......	213	213	231	222	217	218	9.1	43.8
57.......	215	213	215	220	217	218.5	7.3	40.0

a/ Locations numbered progressively further from converter inlet.

In this particular converter, the rows of cooling tubes were staggered, and, in order to increase the heat transfer from gas to tubes, gas flows at both right angles and parallel to the staggered rows were tried. No significant differences were observed, however, in the temperature distribution in the bed.

As the necessary data were obtained from the two converters just described, it was not necessary to construct two other converters that had already been designed. These converters are shown in figures 13 and 14, in which the spacing between the cooling tubes was greater and less, respectively, than in the 3-m.^{3}/hr. converter. That is, the vertical centers were 58 mm. and 43 mm., respectively, and the horizontal centers were 51 mm. and 37.5 mm., respectively.

OUTER-CATALYST CONVERTERS USING WATER AS COOLANT

From the previous experiments with oil-cooled outer-catalyst converters, the minimum allowable spacing between cooling tubes for these conditions was determined. As the final objective was the construction of a water-cooled converter capable of handling 100 m.^{3} of gas per hour, a small unit using water as a cooling medium was built.

Converter With 6-m.^{3}/hr. Throughput

Description of Apparatus

This unit was similar to that shown in figure 5, except that it was designed for a maximum throughput of 6 m.^{3}/hr. and that the oil-cooling

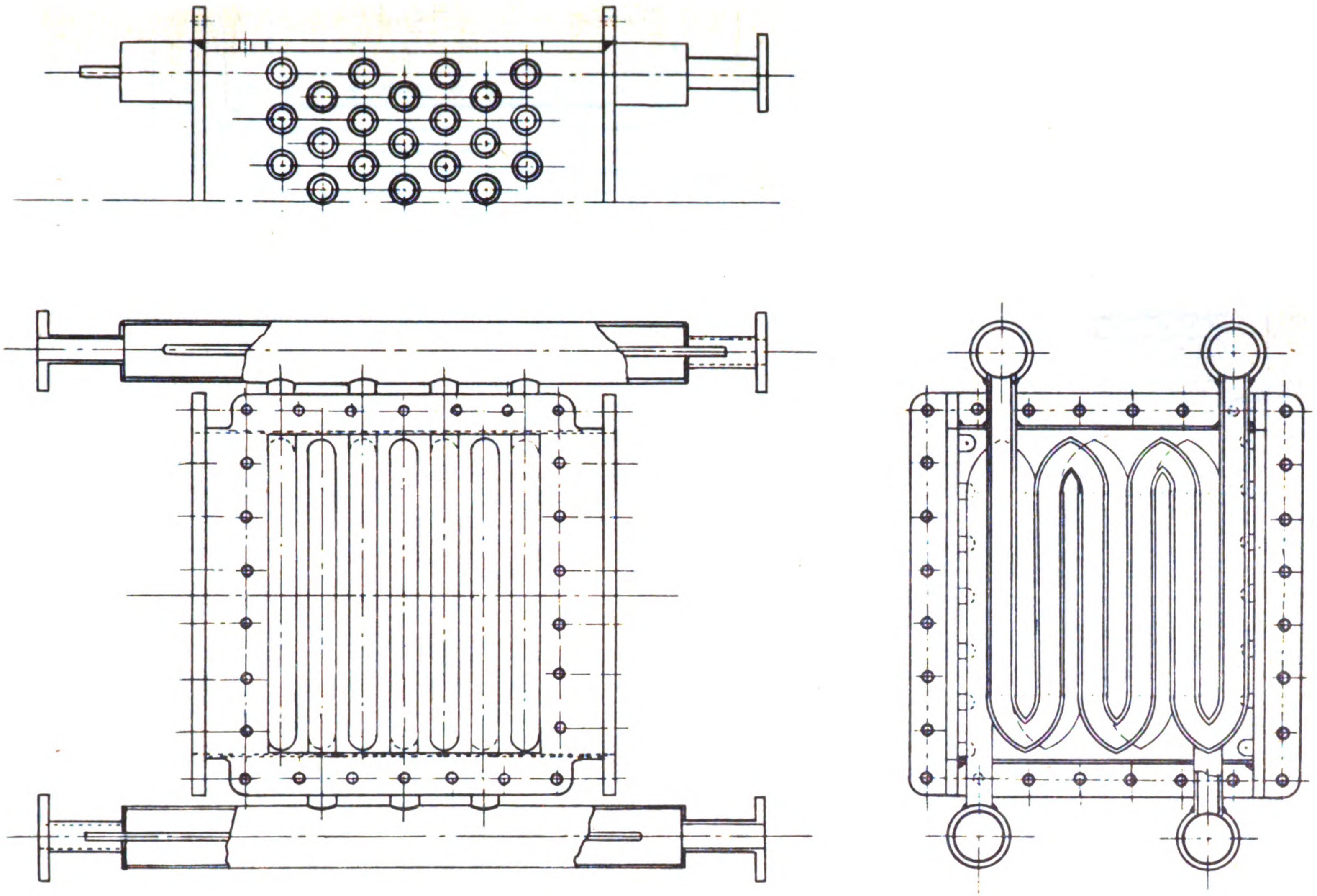


Figure 13. - Proposed outer-catalyst converter (tube centers 58 mm. x 51 mm.).

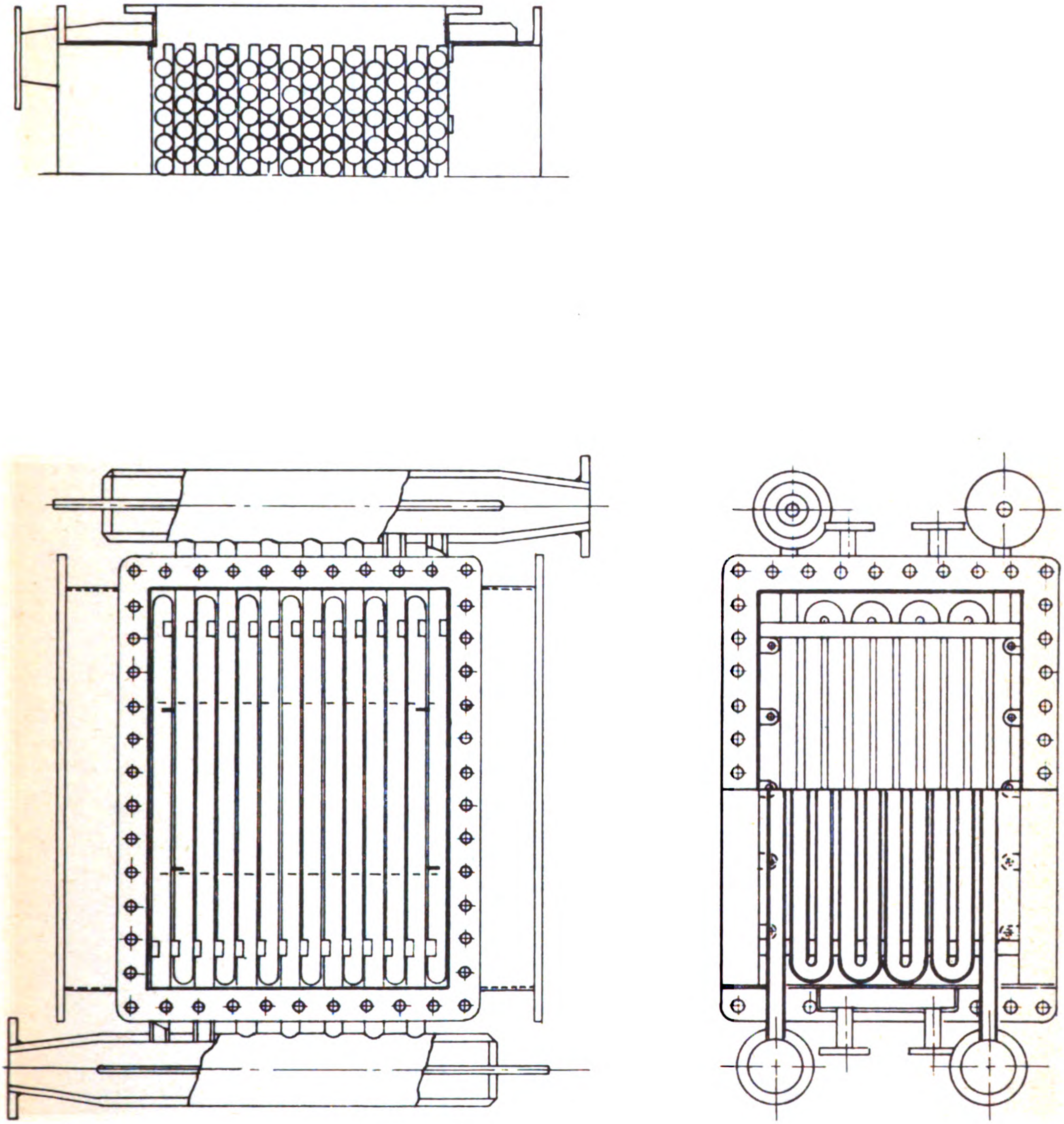


Figure 14. - Proposed outer-catalyst converter (tube centers 43 mm. x 37.5 mm.).

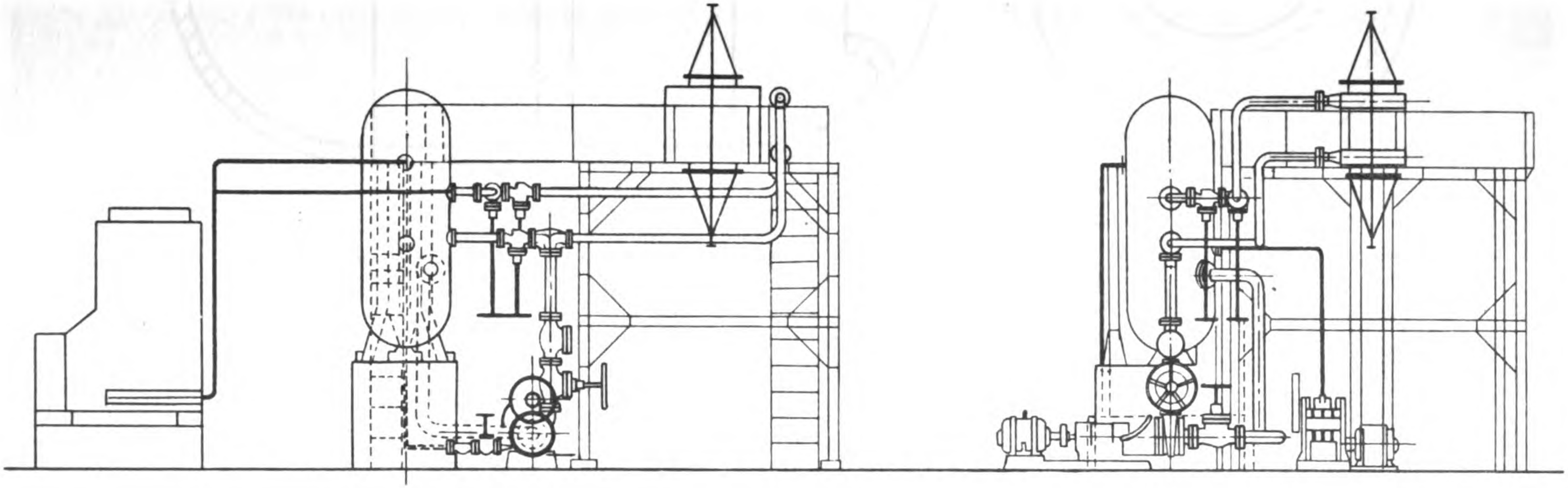


Figure 15. - Hot water circulation apparatus (6 m.^{3}/hr. outer-catalyst converter).

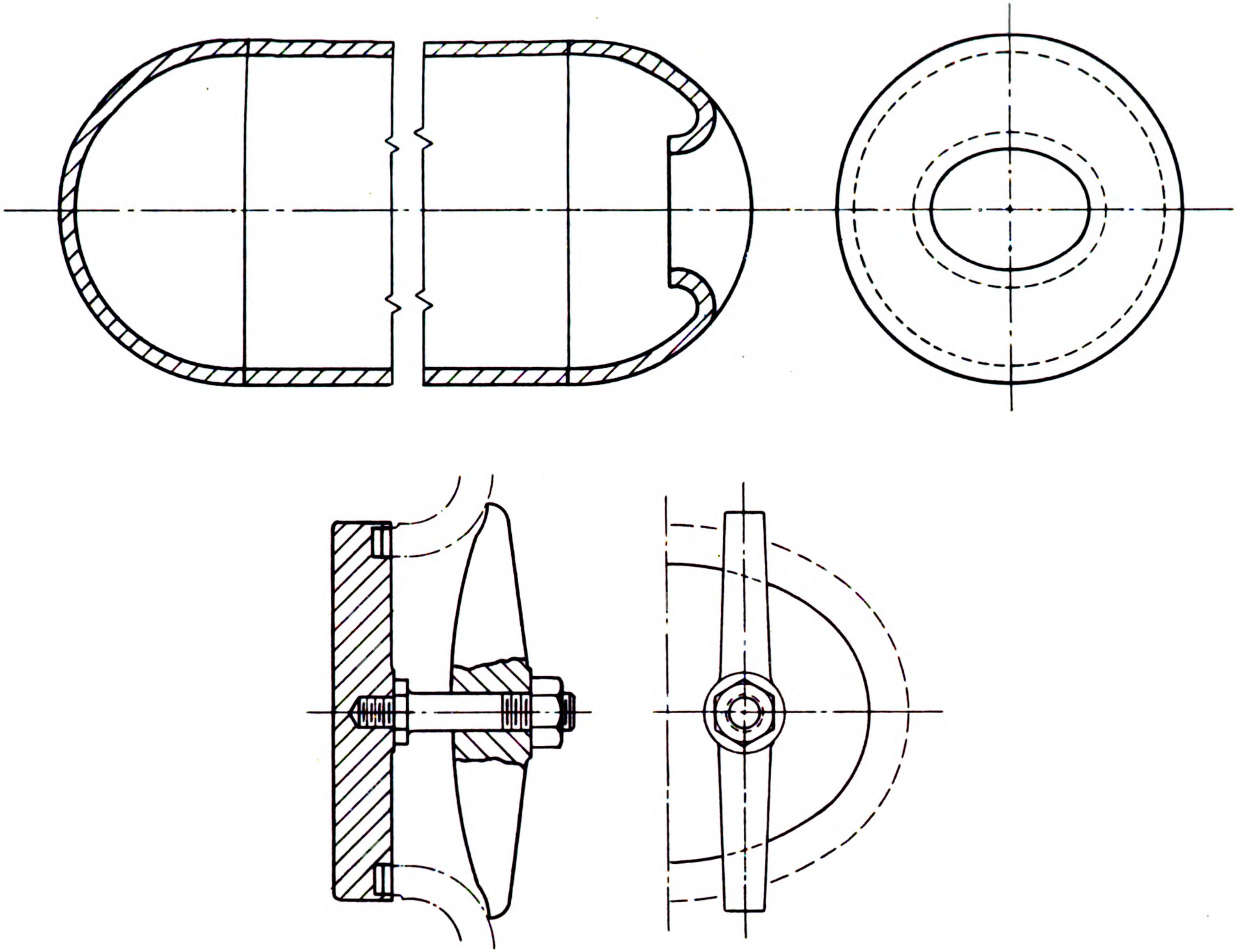


Figure 16. - Hot-water drum (6 m.^{3}/hr. outer-catalyst converter).

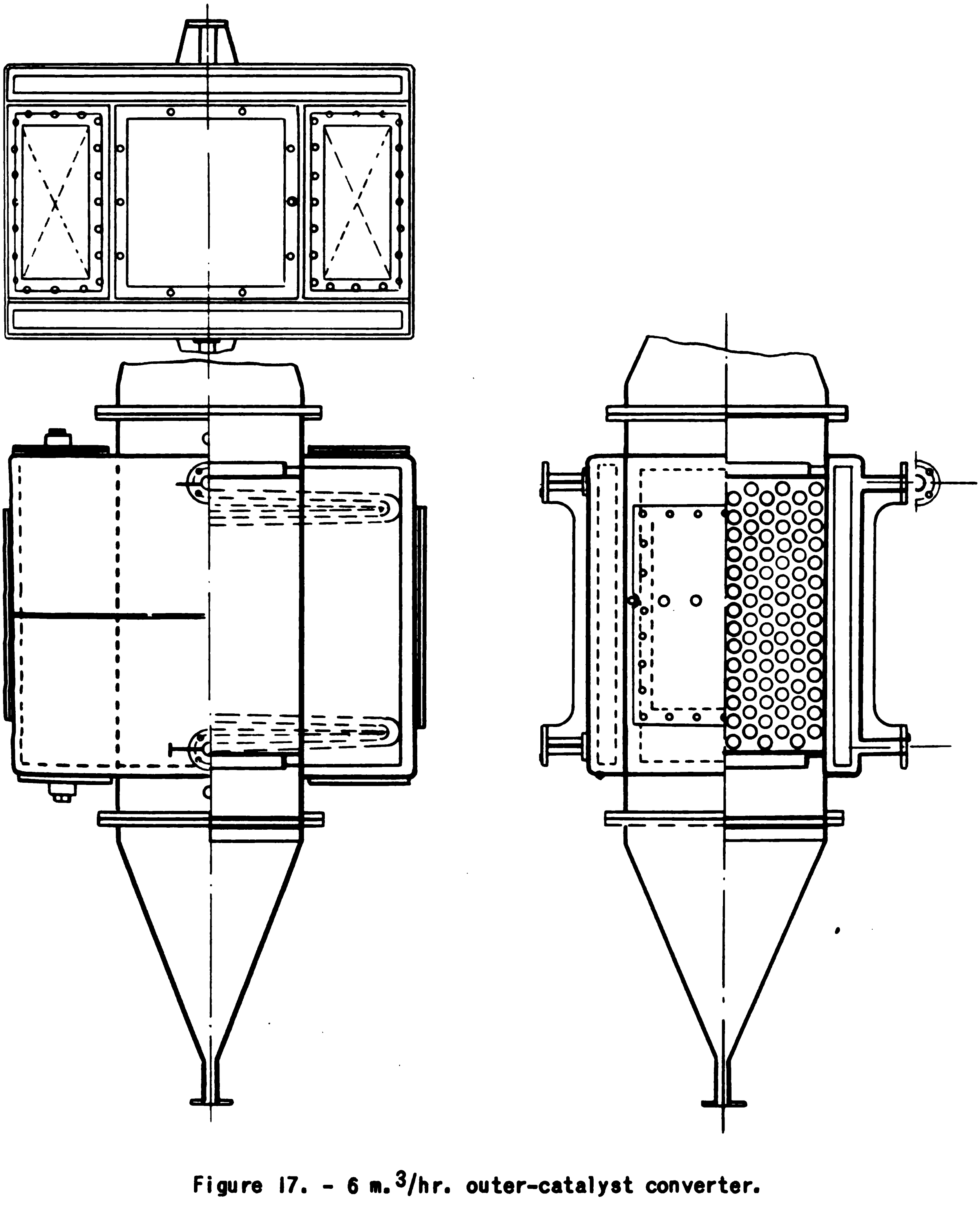


Figure 17. - 6 m.^{3}/hr. outer-catalyst converter.

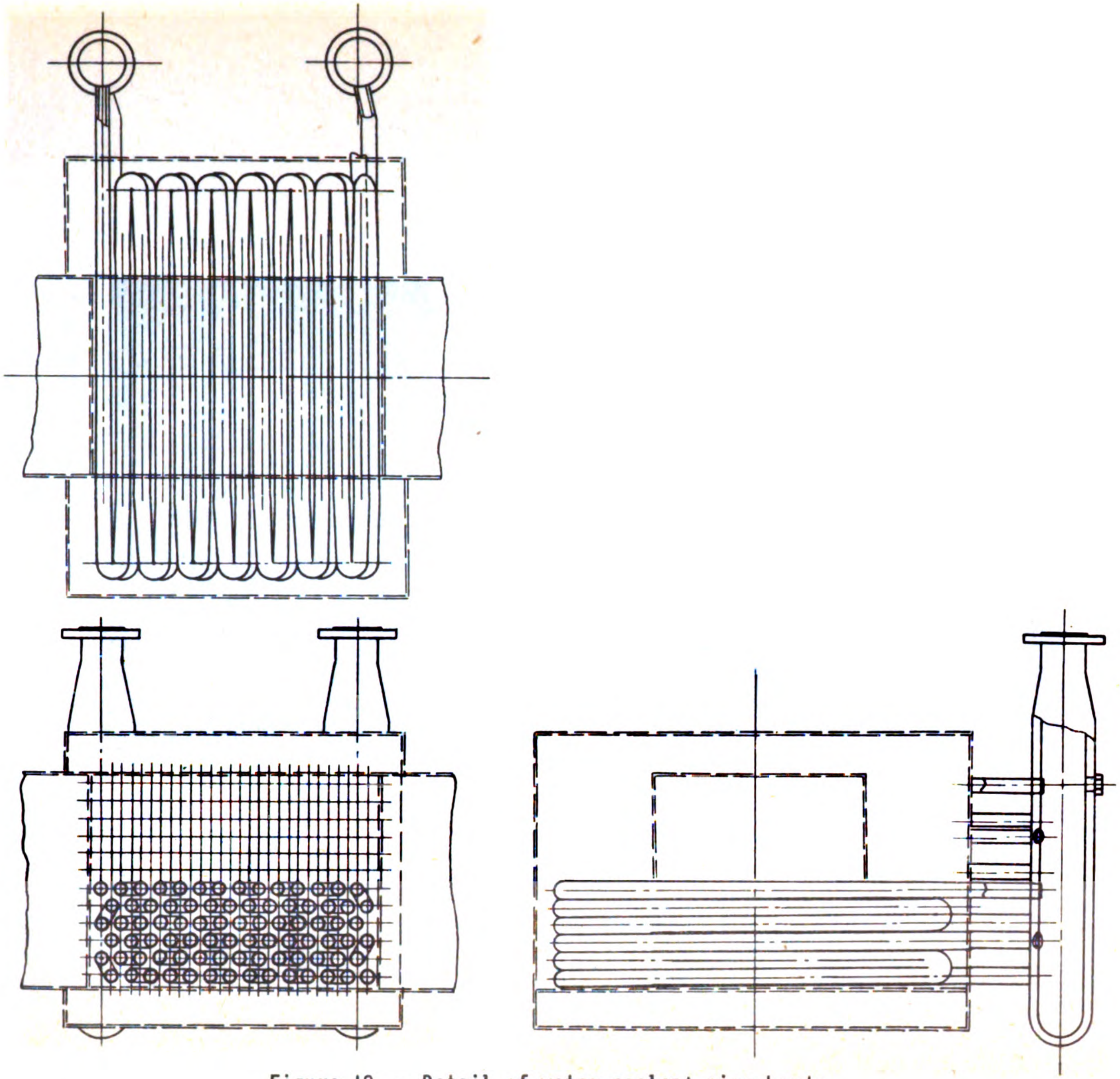


Figure 18. - Detail of water-coolant pipe bends.

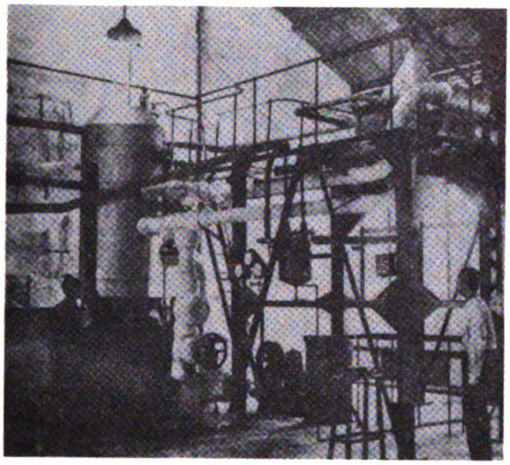


Figure 19. - Hot-water drum, hot water circulation pump and 6 cubic meter per hour outer-catalyst converter.

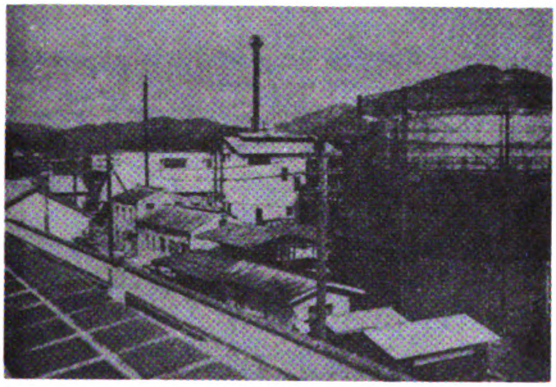


Figure 20. - General view of 100 cubic meter per hour pilot plant.

system was replaced by the water-cooling system shown in figure 15. This system consisted of a water heater, hot-water circulation pump, hot-water storage tank, heat exchanger in converter, and a water-supply pump. The hot water that serves as a coolant is stored in the hot-water drum after the steam has been condensed and the water has cooled in a heat exchanger. The hot water in the drum circulates again by being pumped through the converter.

It was considered desirable to design this apparatus so that it could be used with iron catalysts as well as cobalt catalysts. However, although a hot-water pressure of 10 or 25 atmospheres was sufficient when cobalt catalysts were used at a reaction temperature 180° to 220° C., the use of iron catalysts at their reaction temperature between 230° and 250° C. would require a hot-water pressure of 27 to 40 atmospheres. It was finally decided to use the "Lamont" boiler manufactured by the Kawasaki Heavy Equipment Manufacturing Co.; this company was entrusted thereafter with the construction of all synthesis equipment.

Except for the converter, all the equipment in this experiment was constructed so that it could be adapted to the proposed 100-m.^{3}/hr. unit. Thus, the heater and other auxiliary equipment connected to the hot-water circuit were constructed to withstand a maximum pressure of 50 kg./cm.^{2} and a maximum temperature of 262° C. The hot-water circulating pump had a capacity of 26 tons/hr., receiving water at a pressure of 50 kg./cm.^{2} and delivering it at 53 kg./cm.^{2} Figure 16 shows the construction of the hot-water drum, which, having an inside diameter of 780 mm. and a thickness of 34 mm., was constructed by welding.

The converter, containing tubes 25.6 mm. I.D. and 32 mm. O.D., was designed to hold 60 liters of catalyst. Its 168 cooling tubes were designed to be spaced, originally, on 42.5-mm. vertical centers and 36.5-mm. horizontal centers, but this spacing was decreased slightly in view of the results obtained with the 10-m.^{3}/hr. oil-cooled converter.

One of the difficulties faced in the construction of this converter was, as in the previous experiment, that of making the junctions of the cooling tubes with the reactor wall gas-tight, a natural outcome of packing so many heavy tubes into such a small space. The construction of the converter is shown in figure 17. To eliminate the necessity of constructing so many seals, the bends in the cooling tubes were contained inside the catalyst space as before. The "bends" in the cooling tubes were not formed by actually bending the tubes. Instead, they were constructed, as shown in figure 18, by welding the tubes into cups. As a result, it was impossible to maintain the exact spacing near the "bent" sections of the tubes, and the volumes containing these sections of tubing were separated from the volume packed with catalyst by partitions. As these partitions were not gas-tight, the flow of synthesis gas into the "bent-tube" volumes was inhibited by filling them with diatomaceous earth. To avoid heat losses through the converter walls, the converter was enclosed in an oil bath maintained at the reaction temperatures. Figure 10 shows the Lamont boiler; the hot-water drum, hot-water circulation pump, and converter are shown in figure 19.

Original from THE OHIO STATE UNIVERSITY

Synthesis Operation

Construction of this equipment was completed in September 1939, and a continuous 13-day test was made from September 22 to October 3, using cobalt as catalyst. The results were good. The operation was essentially trouble-free and 99.3 liters of synthesis oil were produced from 1309.1 m.^{3} of gas. After reducing the catalyst and establishing the desired synthesis conditions, an average gas contraction of 54.1 percent and an oil yield of 83 cm.^{3}/m.^{3} of synthesis gas were obtained. Computed on the basis of effective gas in the raw synthesis gas, an oil yield of 104 cm.^{3}/m.^{3} was obtained. This is comparable to the value of 111 cm.^{3}/m.^{3} obtained in the laboratory. The temperatures of the various sections of the converter during the synthesis are shown in table 5. The maximum temperature difference in the catalyst bed was 5° C., indicating that the reaction heat was removed efficiently and that the cooling surface was adequate. The fact that the temperature of this catalyst bed was more uniform than that in the 10-m.^{3}/hr. oil-cooled outer catalyst converter is no doubt, due to the higher thermal conductivity of water compared to oil, as well as to the larger cooling-surface:catalyst-volume ratio.

TABLE 5. - Distribution of temperature in 6 m.^{3}/hr. water-cooled outer-catalyst converter.

Operating time, hours	Water temperature, °C.		Temperature of catalyst bed, °C.					Water pressure, kg./cm.^{2}	Gas flow m.^{3}/hr.	Contraction percent
	In	Out	Upper	Lower	Side	Side	Middle			
8	206	206	205.5	205.5	206	205.5	205	16.2	5.6	7.2
32	207.5	207.5	208	210	210	209	208	17.0	5.5	48.5
56	212	212	215.5	212	218	218	213	18.5	6.1	59.2
80	210	210	213	212	215.5	215	213	18.0	5.3	62.3
104	210	210	212	212	216	216	212	18.0	5.8	54.7
128	210.5	210	212	212	215	215	212	18.0	5.5	59.1
152	210	210	212	212	214.5	214.5	213	18.0	6.1	51.4
176	210	210	211	212	214	214	212	18.0	5.7	49.6
200	210.5	210	212	212	215	215	213	18.1	6.0	45.6
224	210.5	210	212	212	214.5	214.5	212	18.1	4.5	48.1
248	212	212	214	214	216	216	214	18.9	5.4	52.2

Converter With 100-m.^{3}/hr. Throughput

In the preceding experiment, the necessary relationship between cooling-tube spacing and catalyst volume was determined when using water as the coolant. With this information, the design and construction of a 100-m.^{3}/hr. water-cooled outer-catalyst converter was approached. It was expected that, because the 6-m.^{3}/hr. water-cooled converter contained a relatively large ratio of surface area of the reactor wall to volume of catalyst, when a much larger unit was operated in which this ratio was smaller, more internal cooling would be necessary to maintain a uniform catalyst-bed temperature, because the heat lost through the reactor walls by conduction would be proportionately less. Tests with the 100-m.^{3}/hr. converter, however, showed that in this unit such was not the case.

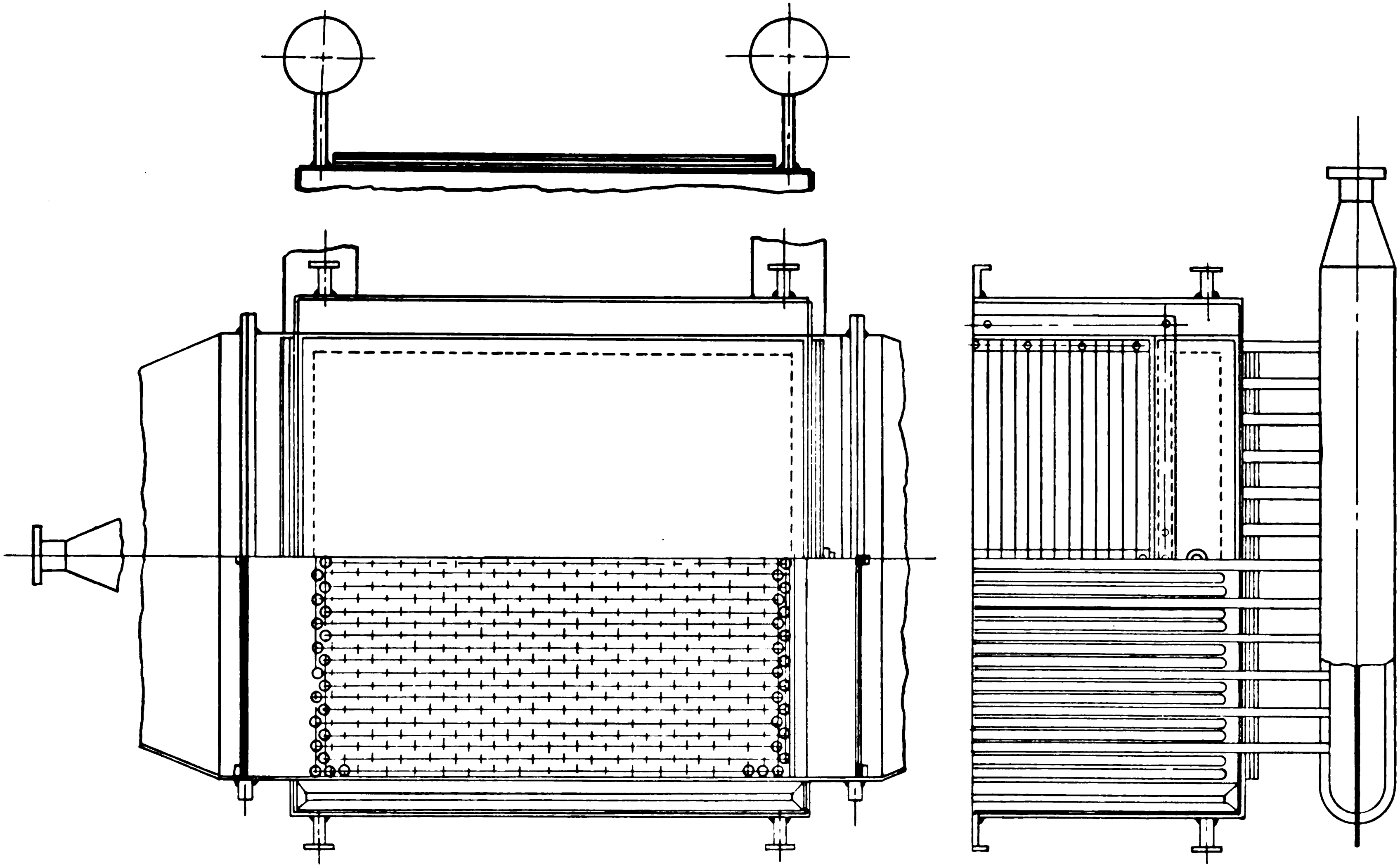


Figure 21. - 100 m.^{3}/hr. outer-catalyst converter (original design).

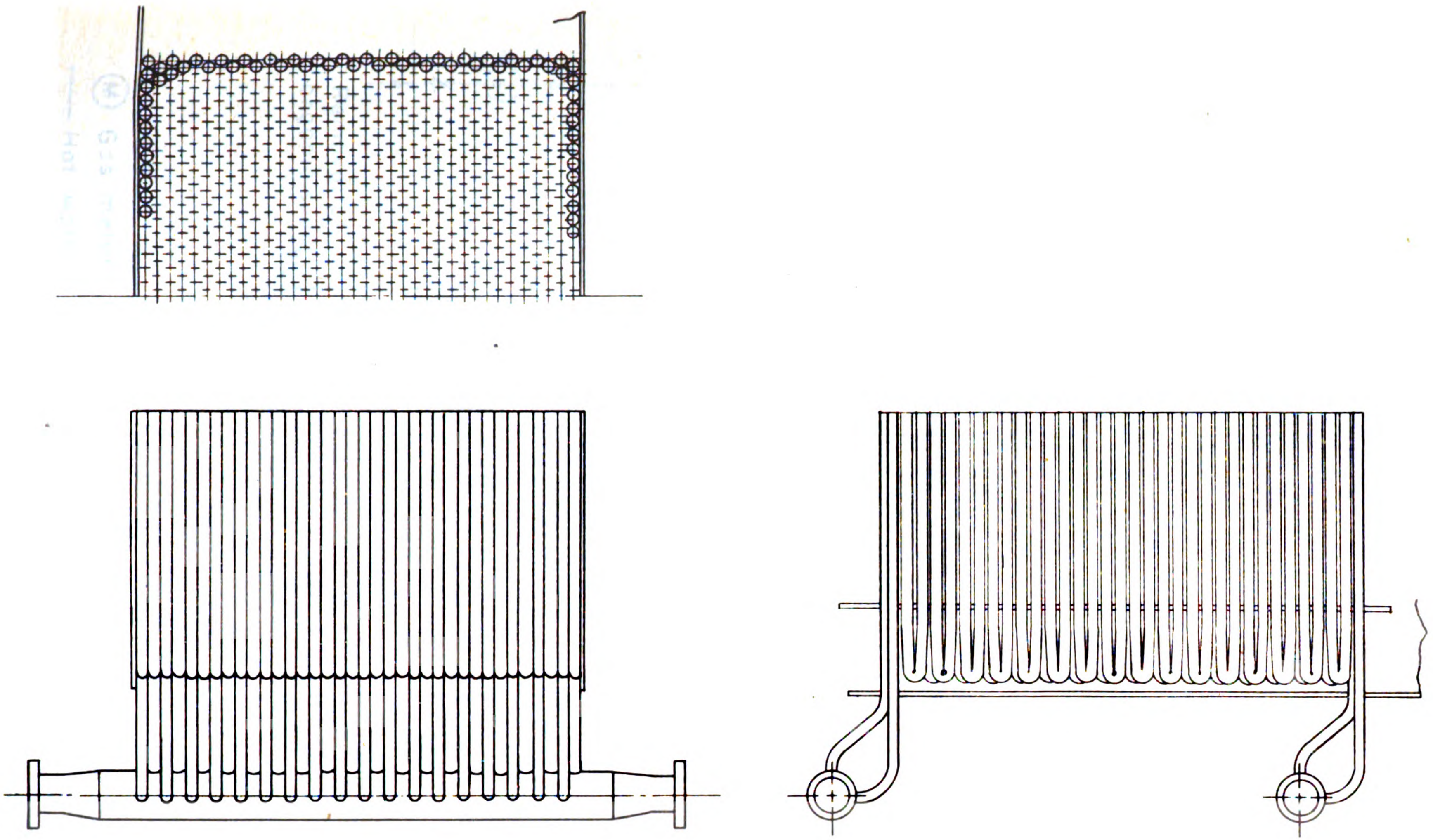


Figure 22. - 100 m.^{3}/hr. outer-catalyst converter (as constructed).

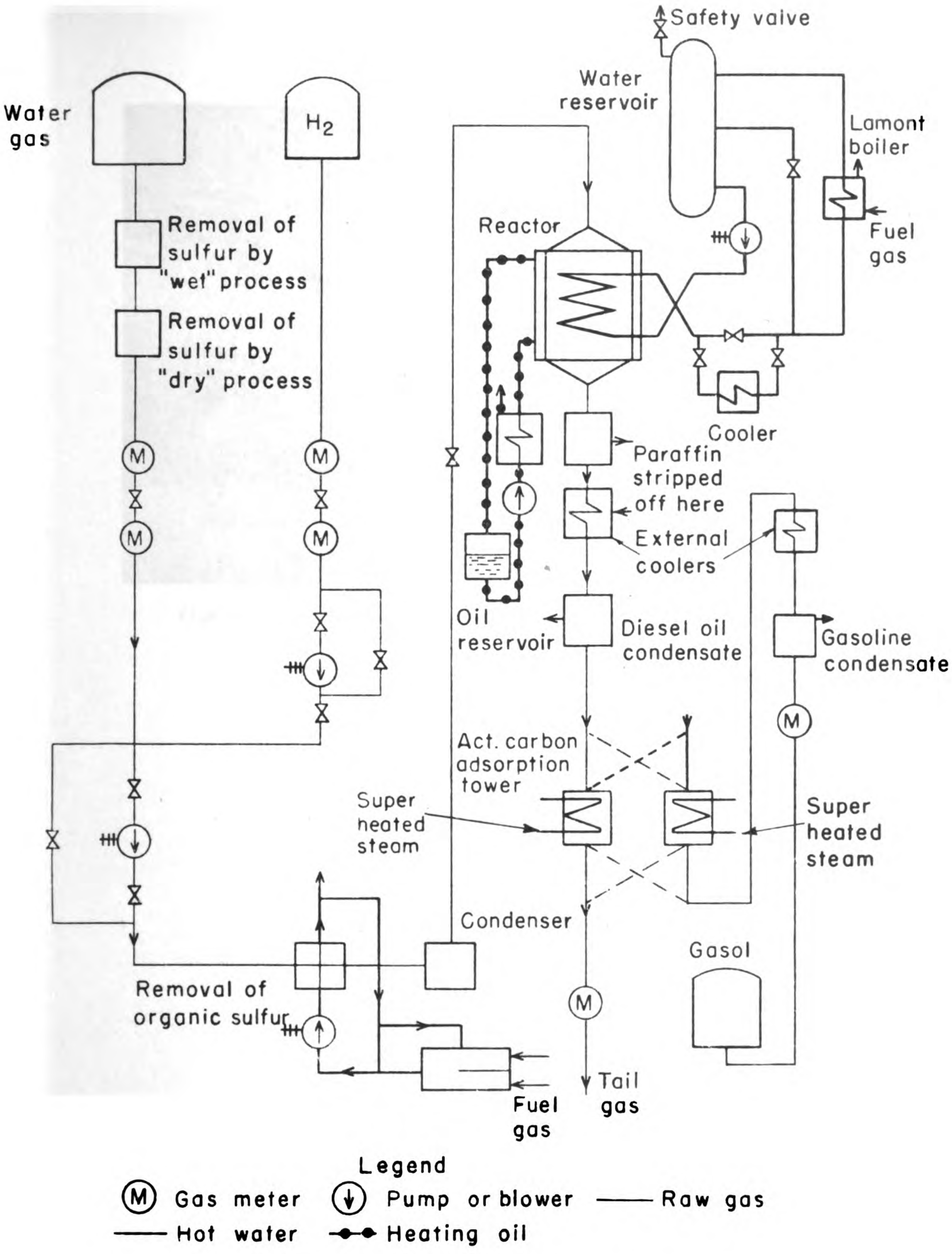


Figure 23. - Flow diagram of pilot-plant process.

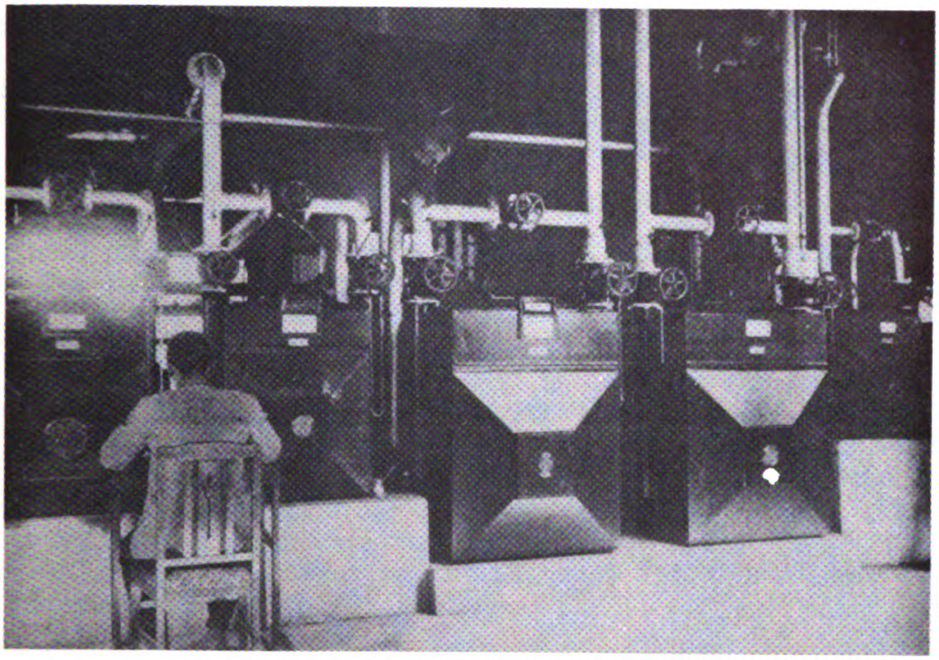


Figure 24. - Gas-meter assembly; (left to right) H_2, water gas, synthesis gas, exit gas, gasol.

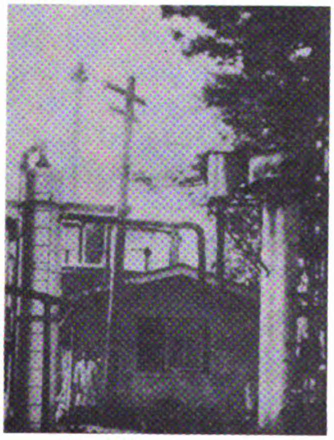


Figure 25. - Wet-type gas desulfurizer: left, washing tower; right, tower for reactivating desulfurizing solution.

Description of Equipment

Figure 21 shows the original design for the 100-m.^{3}/hr. converter. When construction was begun, however, a few changes were made, and figure 22 shows a section of the converter as it was actually constructed. The principle of this design is the same as that of the 6-m.^{3}/hr. converter just described. The tube spacing in the 100-m.^{3}/hr. unit, however, was somewhat greater; 1,224 cooling tubes, having an inside diameter of 25.6 mm. and an outside diameter of 32 mm., were distributed on 42.5-mm. vertical centers and 36.8-mm. horizontal centers.

Figure 20 shows a general view of the oil-synthesis pilot plant. The flow sheet for this pilot plant is shown in figure 23. The product gases emerging from the reactor were stripped of paraffin; after water cooling, the condensed Diesel oil was separated, and the light-oil fraction was adsorbed on activated charcoal. The tail gas was then released to the atmosphere. The light-oil fraction was stripped from the charcoal adsorbers with superheated steam, and the gaseous product was cooled with water to yield a condensate (gasoline) and noncondensable hydrocarbons (C_3+C_4) called "gasol." All equipment used in recovering the product gases from the reactor was designed and constructed especially for this unit. The collection of meters for measuring the flows of the various gas streams is shown in figure 24.

Experimental Procedure; Cobalt Catalyst

Synthesis Gas Preparation

Production of components, CO and H_2. - The use of cobalt catalysts requires a synthesis gas with an H_2:CO ratio of 2:1, and a gas of this composition can be prepared by mixing the proper proportions of water gas and electrolytic hydrogen. A water-gas supply of 400 to 500 m.^{3}/hr. was available from the Osaha Gas Co., which used a low-sulfur coke to produce a water gas similar to the fuel gas supplied to the Kyoto University from the Kyo-Dar plant. Electrolytic hydrogen was produced in a Simmons-type electrolytic cell with a maximum capacity of 23 m.^{3}/hr.

Operation of the water-gas producer at high temperatures was disadvantageous for two reasons. First, it favored the formation of troublesome coke "clinkers," and, second, the H_2:CO ratio of the resulting gas required the addition of electrolytic hydrogen (to meet the required synthesis gas throughput of 100 m.^{3}/hr.) beyond the capacity of the available unit. From these considerations it was decided to produce a water gas containing about 35 percent CO. The gas producers were operated from 9 to 11 a.m. and from 8 to 10 p.m. to yield about 900 m.^{3} of gas during each 2 hour run; this gas was scrubbed with water and stored in a gasholder. The composition of water gas thus obtained is shown in table 6; the gas analyses were carried out in a modified Orsat apparatus, and the sulfur content was determined by burning a sample of the gas, passing the combustion products into sodium carbonate solution, and titrating the remaining sodium carbonate with hydrochloric acid (ASTM method). The hydrogen obtained from the electrolytic cell was washed with water and stored in a gasholder. This hydrogen was about 99.9 percent pure; the impurity was assumed to by oxygen.

TABLE 6. - Composition of water gas

Date, month/day	Time	Hours since start of Experiment 17	Gas composition, volume percent							
									Sulfur, gm./100 m.^{3}	
			CO_2	O_2	CO	H_2	CH_4	N_2	Total	Organic
7/19.....	7 p.m.-10 p.m.	-	9.8	0.2	33.0	48.2	1.7	7.1	16.8	16.5
20.....	9 a.m.-11 a.m.	-	10.2	.0	34.2	47.3	2.5	5.8	12.1	11.9
20.....	7 p.m.-10 p.m.	9-12	7.8	.3	36.5	47.7	1.4	6.3	15.9	15.1
21.....	9 a.m.-11 a.m.	23-25	8.0	.1	36.8	46.8	1.5	6.8	15.2	14.9
21.....	8 p.m.-10 p.m.	34-36	7.2	.1	37.7	48.0	.5	6.5	16.1	15.4
22.....	9 a.m.-11 a.m.	47-49	8.0	.2	36.2	46.0	2.1	7.5	12.7	10.4
22.....	8 p.m.-10 p.m.	58-60	8.5	.2	36.9	46.8	1.4	6.2	14.5	14.0
23.....	9 a.m.-11 a.m.	71-73	9.2	.1	34.7	46.4	2.0	7.6	11.0	10.8
23.....	8 p.m.-10 p.m.	82-84	9.7	.3	35.0	47.4	1.4	6.2	13.1	11.4
24.....	9 a.m.-11 a.m.	95-97	8.7	.2	35.0	48.2	1.4	6.5	14.2	11.9
24.....	8 p.m.-10 p.m.	106-108	8.6	.2	37.8	44.8	1.1	7.5	11.3	10.4
25.....	10 a.m.- noon	120-122	9.5	.0	34.5	47.6	1.1	7.3	15.7	11.0
25.....	8 p.m.-10 p.m.	130-132	8.9	.1	34.6	47.7	2.1	6.6	17.9	12.7
26.....	9 a.m.-11 a.m.	143-145	9.4	.1	34.8	46.9	2.0	6.8	12.1	10.1
26.....	8 p.m.-10 p.m.	154-156	8.8	.2	35.4	48.0	1.8	5.8	10.1	10.0
27.....	9 a.m.-11 a.m.	167-169	8.8	.2	35.0	47.5	1.1	7.4	12.1	11.0
27.....	8 p.m.-10 p.m.	178-180	9.0	.2	34.9	47.5	1.8	6.6	12.9	12.6
28.....	9 a.m.-11 a.m.	191-193	9.6	.2	34.4	46.9	1.1	7.8	12.9	11.4
28.....	8 p.m.-10 p.m.	202-204	8.9	.2	35.4	47.4	1.4	6.7	10.2	10.1
29.....	9 a.m.-11 a.m.	215-217	9.5	.2	35.1	46.3	1.9	7.0	11.6	11.2
29.....	8 a.m.-10 a.m.	226-228	9.8	.2	34.4	46.9	1.8	6.9	13.7	13.1
30.....	9 a.m.-11 a.m.	239-241	9.4	.2	35.8	46.4	1.6	6.6	11.7	10.0
30.....	8 p.m.-10 p.m.	250-252	9.5	.2	34.9	46.5	1.8	7.1	10.4	9.4
31.....	9 a.m.-11 a.m.	263-265	9.2	.2	35.6	46.3	1.6	7.1	12.0	10.7
31.....	8 p.m.-10 p.m.	274-276	9.0	.2	34.9	47.7	1.5	6.7	10.1	9.8
8/1......	9 a.m.-11 a.m.	287-289	8.8	.1	35.9	46.3	1.6	7.3	11.9	10.4
1......	8 p.m.-10 p.m.	298-300	8.8	.1	35.4	47.6	1.5	6.6	12.7	12.1
2......	9 a.m.-11 a.m.	311-313	9.2	.2	34.7	47.9	1.4	6.6	13.4	11.7
2......	8 p.m.-10 p.m.	322-324	9.3	.2	35.1	46.4	1.8	7.2	12.1	10.9
3......	9 a.m.-11 a.m.	-	8.5	.2	35.3	46.8	1.1	8.1	22.8	8.2

Purification and formulation of synthesis gas. - The water gas from the gasholder was first scrubbed to remove hydrogen sulfide in a "wet" process and was then passed through a dry desulfurization chamber containing iron hydroxide and sawdust. Figure 25 shows the wet-type gas desulfurizer with the washing tower on the left and the tower for reactivating the desulfurizing solution on the right. To this purified water gas was then added enough electrolytic hydrogen to yield 100 cubic meters of synthesis gas per hour containing about 84.5 percent of carbon monoxide and hydrogen in a ratio of 1 to 2. This gas mixture was then forced, by means of a blower, through an oven designed to remove organic sulfur from 100 cubic meters of gas per hour (fig. 26). As shown in figure 27, city (fuel) gas was burned in a furnace, and the hot combustion gases were blown over the oven. Inside this oven, the organic sulfur in the synthesis gas was "fixed" by about 800 liters of tablets composed of 20 percent copper, 3 percent caustic soda, and 77 percent diatomaceous earth,

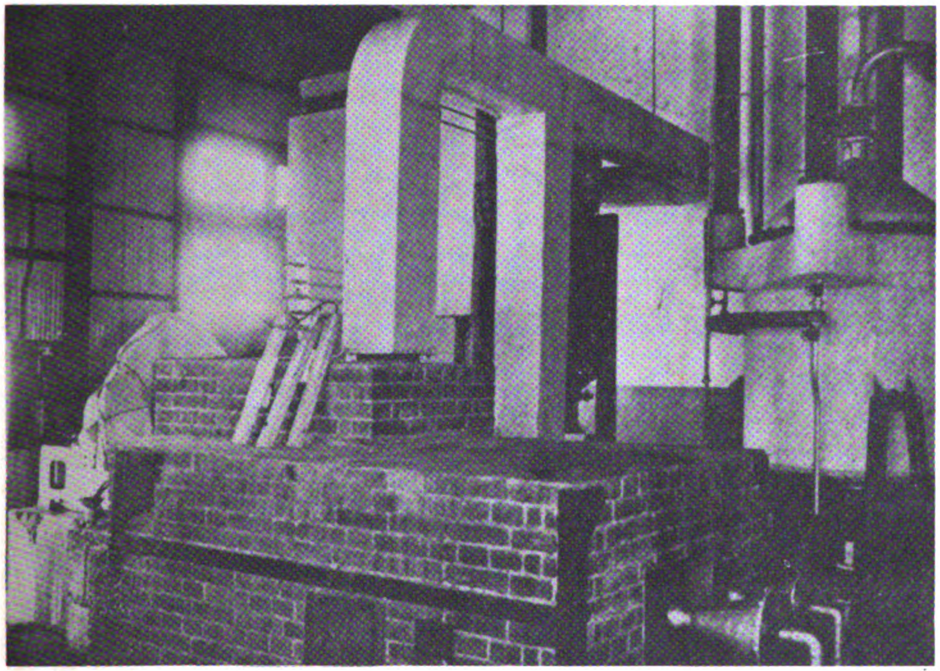
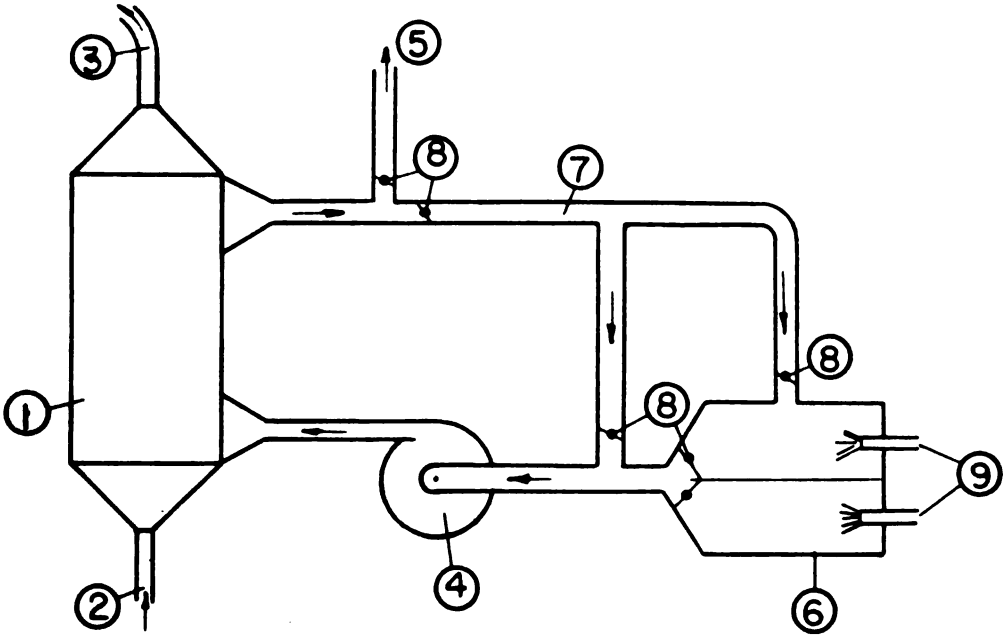
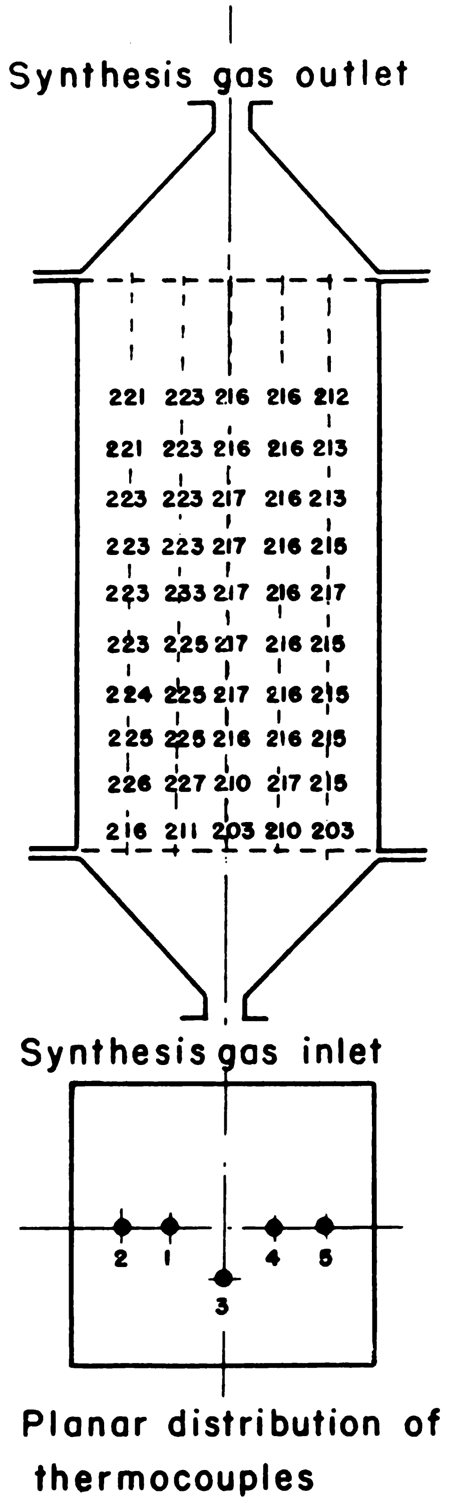


Figure 26. - Apparatus for removing organic sulfur.



1	Furnace	5	Stack
2	Gas inlet	6	Combustion furnace
3	Gas outlet	7	Circulating pipe
4	Gas blower	8	Damper
		9	Fuel gas burner

Figure 27. - Diagram of sulfur-removal system.



221	223	216	216	212
221	223	216	216	213
223	223	217	216	213
223	223	217	216	215
223	233	217	216	217
223	225	217	216	215
224	225	217	216	215
225	225	216	216	215
226	227	210	217	215
216	211	203	210	203

Figure 28. - Temperature distribution in sulfur-removal furnace.

which supplanted the original iron compound (luxmasse-copper hydroxide-alkali) used for this purpose. The compound in use possessed the advantage that, unlike the iron compound, it did not promote side-reactions at high temperatures, resulting in the decomposition of carbon monoxide and the production of methane. By adjusting the blower and the baffle system, a stable temperature distribution of 200° to 220° C. was finally established throughout the mass of sulfur-fixing pellets; this temperature distribution is shown in figure 28. The temperatures existing at points 1 to 5 (fig. 28) and the inlet and outlet temperatures of the combustion products are listed in table 7 along with the sulfur contents of the emerging synthesis gas; a gradual increase in the latter can be observed. The small amount of sulfur present in the emerging synthesis gas was determined by converting it to barium sulfate.

TABLE 7. - Removal of organic sulfur from synthesis gas

Date, month/day	Time	Hours since start of experiment 17	Temperature distribution in oven, °C.							Sulfur content of emerging synthesis gas gm./100 m.^{3}
			Combustion products		Thermocouples[a]					
			Inlet	Outlet	1	2	3	4	5	
7/19.....	1 a.m.-4 a.m.	-	233	195	223	226	219	219	214	<0.07
20.....	1 a.m.-5 a.m.	-	240	203	230	227	226	220	220	$<.07$
21.....	Midnight-4 a.m.	14-18	240	206	233	233	227	227	226	.09
22.....	1 a.m.-5 a.m.	39-43	240	204	233	233	230	226	226	.12
23.....	1 a.m.-5 a.m.	63-67	240	203	233	233	227	230	230	.07
24.....	2 a.m.-6 a.m.	88-92	240	200	233	233	227	230	226	.15
25.....	11 p.m.-10 a.m.	133-144	226	197	218	218	212	212	212	.09
26.....	10 p.m.-6 a.m.	156-164	226	198	222	218	213	209	202	.15
27.....	11 p.m.-6 a.m.	181-188	230	205	218	222	215	215	206	.16
28.....	10 p.m.-5 a.m.	204-211	226	198	218	216	213	210	205	.20
29.....	10 p.m.-6 a.m.	228-236	230	198	218	219	212	213	206	.20
30.....	10 p.m.-7 a.m.	252-261	230	197	217	219	213	213	206	.22
31.....	10 p.m.-6 a.m.	276-284	230	197	217	219	210	214	204	.30
8/1.....	10 p.m.-6 a.m.	300-308	230	197	217	219	210	213	204	.34
3.....	Midnight-6 a.m.	326-332	230	194	218	220	213	215	206	.25

[a] See figure 4.

Catalyst

The activity of the pelleted catalyst (100Co:10Cu:5ThO_2:2.5U_3O_8:125 diatomaceous earth), 960 liters of which was used in experiment 17, was determined by testing in an electrically heated reactor with 2H_2:1CO gas. The testing conditions and the analyses of the product are listed in table 8.

TABLE 8. - Catalyst activity

(Catalyst composition = 100Co:10Cu:5ThO_2:2.5U_3O_8:125 diatomaceous earth)

Converter temperature, °C.	Operating periods	Length of operation, hours	Gas flow, l./hr.	Contraction, percent	Liquid products, ml./m.^{3}			
					H_2O	Diesel oil	Gasoline	Total oils
200.........	1	17.0	3.8	26.5	45	9	19	28
200.........	2	20.0	4.1	76.7	182	68	60	128
200.........	3	23.0	3.9	73.3	179	69	63	132
200.........	4	23.0	4.0	69.6	162	61	55	116
210.........	1	17.0	3.9	75.3	159	33	31	64
210.........	2	20.0	3.9	76.5	180	55	52	107
210.........	3	23.0	3.9	74.6	178	56	55	111
210.........	4	23.0	3.8	72.6	169	49	60	109
210.........	5	23.0	3.9	68.8	161	45	56	101
210.........	6	23.0	3.9	64.6	148	38	59	97
210.........	7	23.0	4.3	60.0	138	36	53	89
215.........	1	17.0	3.7	75.8	166	37	52	89
215.........	2	20.0	4.0	75.9	183	49	62	111
215.........	3	23.0	4.2	72.4	166	45	57	102

Synthesis Operation

At 8:00 a.m. on July 17, the production and purification of synthesis gas was begun. At 2:00 a.m. on July 18, when the organic sulfur content was less than 0.07 gm./100 m. of synthesis gas, the Lamont boiler was placed in operation to supply heat to the reaction furnace, and synthesis gas was directed through the furnace at a velocity of 100 m.^{3}/hr. The temperature of the catalyst charge was raised slowly until, at 10:00 a.m. on July 19, an apparent contraction of 14.8 percent was obtained at 195° C.; 12 hours later an apparent contraction of 21.5 percent was obtained at 200° C., and, after a subsequent 12-hour period, 46.2 percent was obtained at 201° C. This point (10:00 a.m., July 20) was considered as zero time in computing the operating life of the experiment; 202 l. of water, 5 l. of Diesel oil, 33 l. of gasoline, 17 m.^{3} of gaseous hydrocarbons, and no paraffin having been produced up to this time, the reduction of the catalyst was now considered complete.

From this point on, during the operating life of the experiment, the converter temperature and the gas flow rate were measured every hour; samples of the synthesis gas and the gaseous hydrocarbon products were taken for analysis every 2 hours. The instrument panel is shown in figure 29. The activated carbon-adsorption chambers were alternated every 24 hours, and the adsorbed products were recovered. At this time the total production was determined; paraffins, Diesel oil, and gasoline were stored in tanks, and gasol was stored in a gasholder.

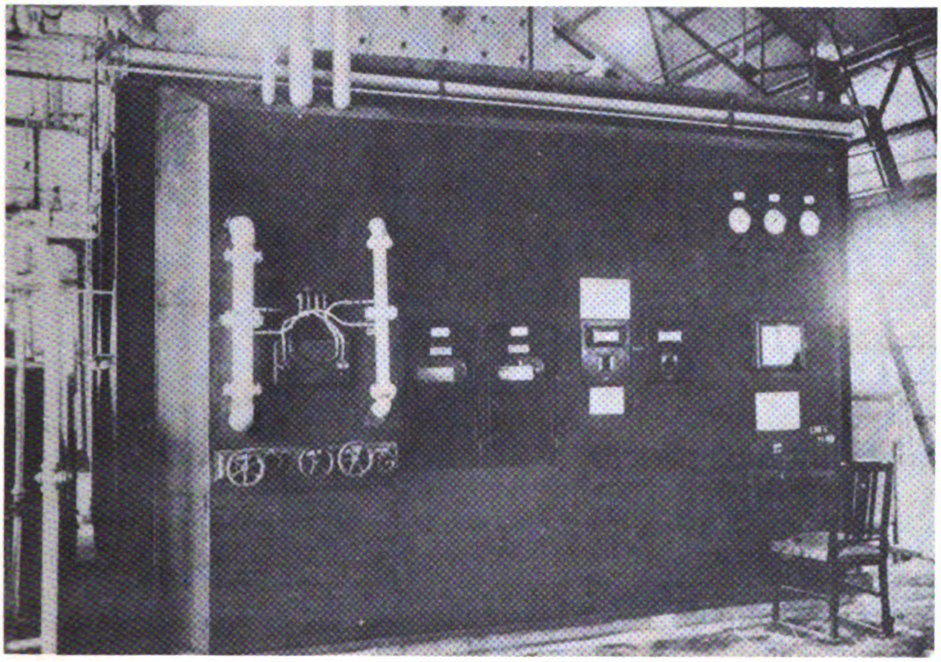


Figure 29. - Instrument panel.

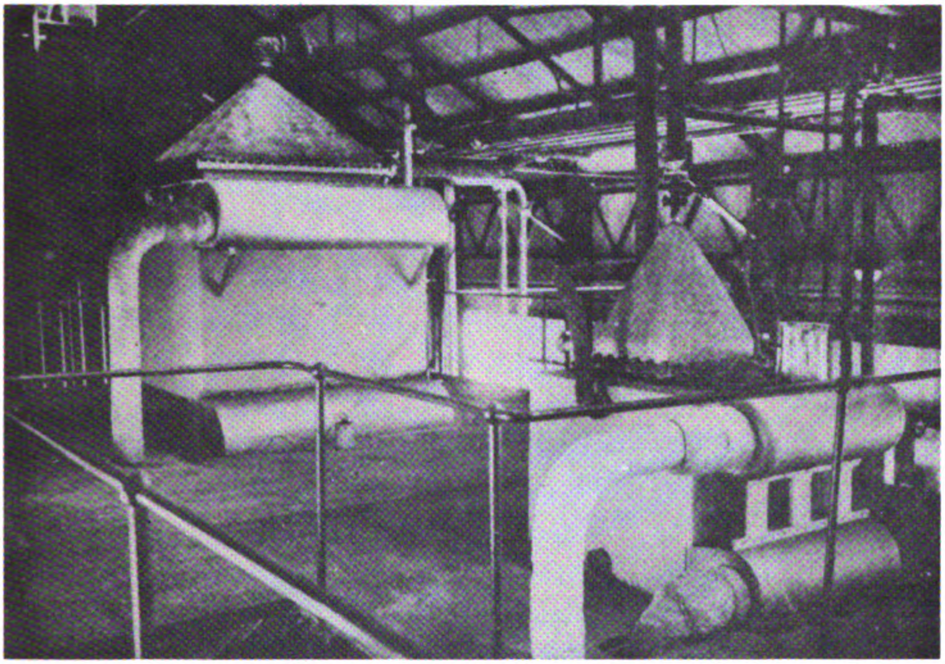


Figure 30. - Water-cooled reactors: foreground, 6 cubic meter per hour unit; background, 100 cubic meter per hour unit.

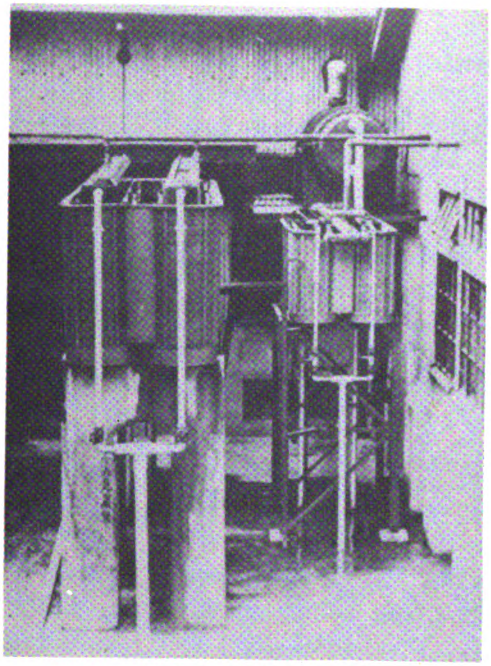


Figure 31. - Heat exchangers: left, Diesel-oil cooler; right, gasoline cooler.

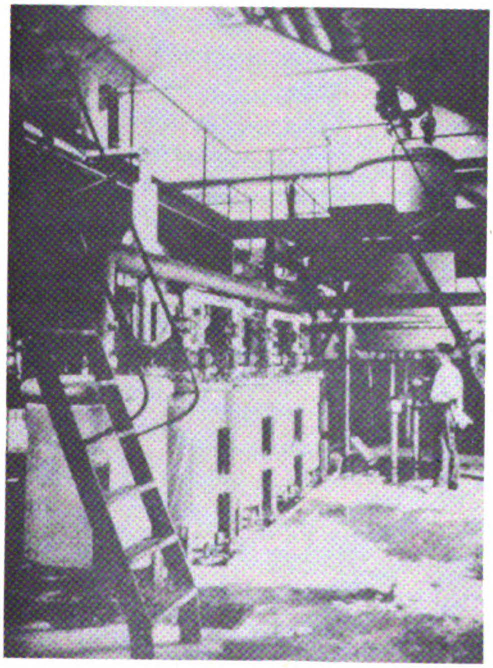


Figure 32. - Foreground, Diesel-oil separators; background, activated-carbon tower for adsorbing light oil.

Discussion of Results

The highest yields in experiment 17 were obtained during the first 48 to 72 hours, when the temperature of the steam entering the heating jacket of the converter was 201° to 202° C.; a maximum yield of 302 l. of water and 192 l. of primary liquid product (oil) was obtained. During the first 24 hours of operation, an apparent contraction of 58.2 percent was observed with the production per cubic meter of synthesis gas of 160 ml. of water, 103 ml. of oil, and 10 l. of gasol; correction for the inerts content of the synthesis gas gives an actual contraction of 66.5 percent and corresponding product values of 180 ml. of water, 120 ml. of oil, and 12 l. of gasol per cubic meter of pure $2H_2:1CO$ gas. The activity of the pilot-plant catalyst, therefore, was comparable to the activities found in small, bench-scale tests. To compensate for a gradual loss in catalyst activity, the operating temperature was gradually increased from 200° to 215° C.; after continuous operation for 336 hours, experiment 17 was terminated. Photographs of the reactor and auxiliary equipment are shown in figure 30, 31, and 32.

The results of experiment 17 are listed in table 9. For an average apparent contraction of 56.2 percent, a total production of 4,488 l. of water, 258 l. of paraffin hydrocarbons, 538 l. of Diesel oil, and 1,472 l. of gasoline (2,288 l. total oil) were obtained from 26,729 m.^{3} of synthesis gas. Calculations showed that the actual synthesis gas velocity during the experiment averaged only 79.6 m.^{3}/hr. instead of the 100 m.^{3}/hr. indicated by the gas-meter. The difference may be attributed to meter calibration, temperature, and pressure corrections, and to a slight gas leak at the exit of the blower. Incorporating this correction into previous calculations produced the following average results per cubic meter of synthesis gas:

4056

Original from THE OHIO STATE UNIVERSITY

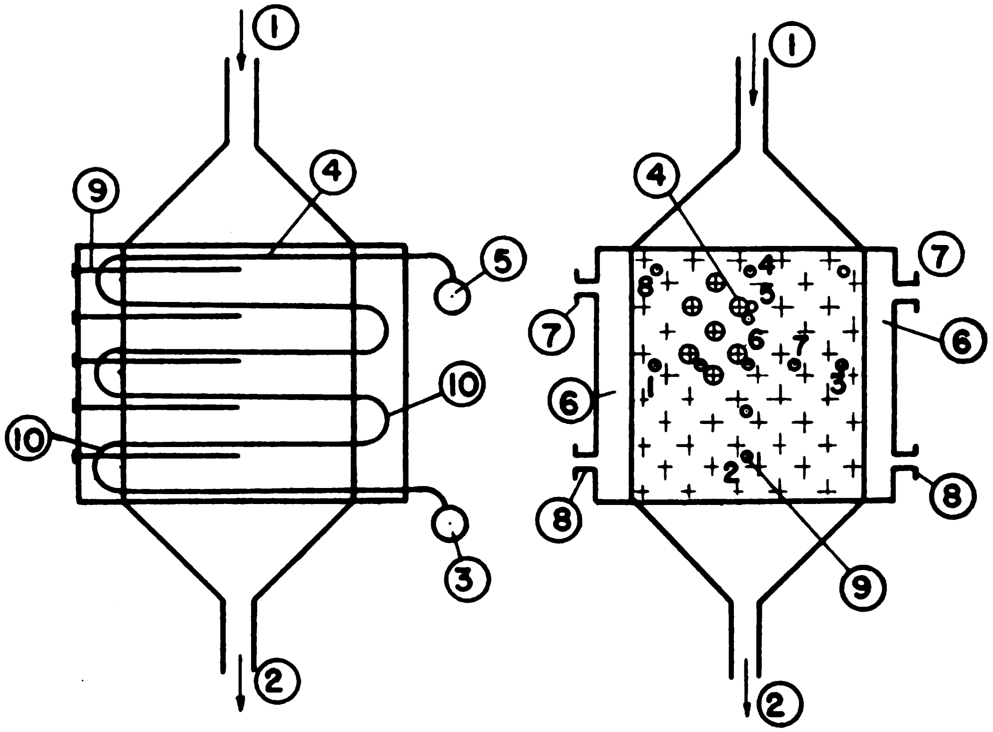
TABLE 9. - Results of Experiment 17

Experiment life, days	Hot H_2O, °C.	Reaction temperature, °C.	Volume of synthesis gas used, m.3	Gas velocity, m.3/hr.	Contraction, percent	Liquid products, liters/day					Gasol, m.3/day	Gaseous products, ml./m.3		
						H_2O	Paraffin	Diesel oil	Gasoline	Total oil		H_2O	Oil	Gasol
1........	201.5	202.5	1,837	76.5	52.4	285	19	32	83	134	19	155	73	10
2........	202	204.5	1,872	78.0	58.2	315	22	44	97	163	21	168	87	11
3........	202	206.5	1,865	77.7	58.2	302	35	47	110	192	18	160	103	10
4........	202	207	1,859	77.4	57.7	307	23	45	105	173	13	165	93	10
5........	203	207	1,832	76.4	58.6	299	22	43	105	170	17	163	93	9
6........	203	208.5	1,848	77.8	55.1	295	22	42	103	167	15	160	90	8
7........	206	210	1,843	76.8	60.8	321	19	43	110	172	12	174	91	7
8........	207	211	1,815	75.6	61.9	311	17	43	110	170	16	171	94	9
9........	208	212	1,974	82.3	58.6	343	16	41	113	170	10	174	86	5
10........	209	212.5	2,009	83.3	55.3	355	14	40	110	164	14	177	82	7
11........	209	213	1,990	82.9	54.7	343	13	36	108	157	10	172	79	5
12........	210	213.5	1,979	82.4	53.2	342	13	37	112	162	11	173	82	5
13........	211	213	2,005	83.5	53.2	339	12	33	110	155	9	169	77	4
14........	211	214	2,001	83.4	50.3	331	11	32	96	139	10	165	70	5
Total.....	-	-	26,729	-	-	4,488	258	558	1,472	2,288	-	-	-	-
Average...	-	-	-	79.6	56.2 a/(66.5)	-	-	-	-	-	14.5	168 a/(199)	86 a/(102)	7 a/(8)

a/ These values computed on basis of inert-free synthesis gas.

4056

Original from THE OHIO STATE UNIVERSITY



1. Synthesis gas inlet
2. Outlet for product gas and unreacted synthesis gas
3. Cooling water distributor
4. Cooling tubes
5. Hot water collector
6. Heating jacket
7. Outlet from heating jacket
8. Inlet to heating jacket
9. Thermocouple tubes
10. Cooling tube return bends

Points 1,2,3,4,5,6,7 and 8 designate points of temperature measurement.

Figure 33. - Thermocouple locations in 100 m.^{3}/hr. converter.

Synthesis gas containing 15.5 percent inert gases: 168 ml. water, 86 ml. oil, 7 l. gasol.

Inert-free synthesis gas: 199 ml. water, 102 ml. oil, 8 l. gasol.

The heating schedule for the catalyst bed is shown in table 10, and simultaneous temperatures at different points in the heating jacket are listed in table 11 (the location of these points is shown in figure 33).

4056

Table 10.- Temperature schedule in catalyst bed[a]

Experiment life, hours	Steam temperature, °C.		Catalyst bed temperature, °C.								Synthesis gas velocity, m.^{3}/hr.	Apparent contraction, percent
	In	Out	1	2	3	4	5	6	7	8		
0	199	198	200	200.5	199.5	200.5	202.5	200	200.5	201.5	86.5	22.5
4	200	201.5	200	200	200	202.5	204.5	200	202	204.5	87.6	54.9
16	201.5	202	204	201.5	201.5	206.5	206.5	201.5	205	205	86.9	54.0
28	202.5	203	201.5	192.5	199.5	204	206.5	204.5	202	206.5	84.5	57.3
40	201.5	201.5	203.5	194.5	201	203.5	206.5	203.5	203.5	204.5	89.4	56.2
52	202	203	204	193	201.5	204	206.5	204	204.5	204.5	88.0	60.2
64	202	203	208	206.5	206.5	206	207	204	206.5	206	86.6	56.4
76	202	203	207.5	207.5	208.5	204.5	207	204	206.5	205	84.9	58.0
88	202	202	209	209	206.5	206.5	206.5	204	204	204	86.4	56.4
100	202	203	207	206.5	206	204	205.5	204	206.5	206	90.4	58.5
112	203	204	206	206.5	206.5	206.5	206	204	205	204	83.1	58.3
124	203	204.5	208	208	206.5	206.5	207	205	206	204	89.9	60.5
136	203	203.5	206.5	206.5	206.5	205	207	204	206.5	205	87.6	52.1
148	206	206	210.5	211.5	209.5	209	211.5	206.5	211.5	209.5	88.8	62.3
160	206	206	211.5	211.5	209.5	209.5	211.5	208	211.5	210	88.1	57.6
172	207	208	212	211.5	211	211.5	212	209	213	209	81.2	59.3
184	207	207.5	210.5	210.5	208.5	207	211.5	208.5	210.5	207	88.6	56.3
196	208.5	209	213	212	211.5	209.5	213	209	211.5	210	96.0	55.2
208	208	209	211.5	211.5	211	209.5	213	209	212.5	209.5	96.6	52.0
220	209	210	214.5	215.5	213	211.5	214.5	210	213	211.5	94.0	58.0
232	209	209.5	212	211.5	210	209.5	214	211.5	211.5	209.5	92.6	52.5
244	208.5	209	214.5	212	211.5	211.5	215.5	212	211.5	209.5	91.5	58.6
256	209	209.5	214	211.5	209.5	210	214	210.5	210	209	93.2	52.5
268	210	211	215	214.5	212	214.5	215.5	211.	211.5	211.5	93.8	55.3
280	210	210.5	215.5	214.5	211.5	211.5	214.5	212	211.5	210	91.7	49.0
292	211	212	214.5	213	211.5	211.5	214	213	213	211.5	92.8	53.7
304	211	211.5	214.5	214	211.5	211.5	214.5	213	211.5	211	92.5	54.1
316	211	211	214.5	213.5	211.5	211.5	214	213	211.5	211.5	94.0	53.5
328	211	211.5	214	211.5	211.5	210	214.5	213.5	211.5	210	93.3	48.0

a/ No corrections made for temperature.

TABLE 11. - Temperature distribution in converter

Distance from center, cm.[a]	Points of temperature measurement[b]					
	1	2	4	5	7	8
0	216	214	209.5	214.5	214.5	211.5
10	217	211.5	211.5	214.5	214.5	211.5
20	216.5	212	212.5	214.5	214.5	211.5
30	215.5	213	213	214.5	214.5	211.5
40	215.5	214	213	214.5	214.5	212
50	215.5	211.5	213	214.5	213.5	214.5

[a] Temperatures measured at points moving progressively from center toward cooling coil bends (see fig. 1).

[b] Distribution of thermocouple locations shown in figure 1.

The analyses of samples of the gaseous mixture leaving the converter are listed in tables 12 and 13 and indicate that the extent of side reactions has been small. Comparison of these results with those of small, bench-scale experiments (table 14) indicates that more satisfactory yields are obtained in a large-scale operation. These results suggest that commercial synthesis of gasoline and hydrocarbon oils from carbon monoxide and hydrogen will be successful.

4056

Table 12.- Synthesis- and product gas analyses.

Experiment life, hours	Synthesis gas, volume-percent							Product gas, volume-percent						
	CO_2	O_2	CO	H_2	C_nH_{2n+2}	N_2	"Useful gas"	CO_2	O_2	C_mH_n[a]	CO	H_2	C_nH_{2n+2}	N_2
0	7.2	0.3	28.4	54.9	2.3	6.9	82.4	14.0	0.1	0.0	21.5	45.0	9.3	10.1
5	7.7	.1	27.4	56.3	2.2	6.3	82.2	19.4	.0	.2	19.4	39.2	12.1	9.7
17	5.2	.1	30.4	56.0	1.8	6.5	84.0	13.1	.0	.2	24.8	41.0	9.3	11.6
29	6.1	.1	28.7	56.5	1.6	7.0	84.8	16.9	.0	.4	21.3	35.4	12.9	13.1
41	6.2	.2	29.0	56.8	1.9	5.9	85.2	14.9	.1	.4	24.0	36.8	12.7	11.1
53	6.0	.2	28.2	57.5	1.5	6.6	84.6	17.0	.1	.3	22.3	27.7	11.8	10.8
65	6.3	.2	28.2	57.9	1.0	6.4	84.6	16.5	.2	.7	21.4	37.6	14.1	9.5
77	7.3	.1	26.9	57.2	1.5	7.0	80.7	19.9	.3	.3	19.4	37.9	12.1	10.1
89	7.0	.2	27.6	55.3	2.0	7.9	82.8	16.6	.2	.6	19.8	37.6	13.8	11.4
101	7.4	.1	28.9	56.5	1.3	5.8	84.7	18.2	.2	.3	22.2	37.2	11.5	10.4
113	6.7	.1	27.0	57.5	1.7	7.0	81.0	17.0	.2	.9	17.2	36.6	16.5	11.6
125	7.4	.2	26.4	56.2	1.5	8.3	79.2	18.6	.1	.4	21.0	36.1	11.7	12.1
137	7.2	.1	28.4	55.6	1.6	7.1	83.5	15.2	.1	.7	23.5	37.9	12.1	10.5
149	7.4	.2	27.7	53.5	2.9	8.3	80.3	22.8	.3	.4	15.2	29.1	18.5	13.7
161	7.0	.1	28.6	57.5	1.3	5.5	85.8	18.1	.1	.5	19.9	30.7	19.4	11.3
173	6.8	.2	28.8	54.8	2.6	6.8	82.2	21.2	.0	.4	18.0	29.0	19.0	12.4
185	7.1	.1	28.0	57.1	1.5	6.2	84.0	18.3	.0	.8	18.8	30.4	20.5	11.2
197	7.6	.2	27.5	56.9	1.6	6.2	82.5	20.6	.1	.5	16.8	34.0	17.4	10.6
209	7.0	.1	28.3	56.8	1.3	6.5	84.9	16.5	.0	.6	20.6	36.6	17.1	8.6
221	7.9	.2	27.7	55.8	2.6	5.8	83.1	20.8	.1	.2	16.7	32.0	18.6	11.6
233	7.5	.1	27.9	56.0	1.9	6.6	83.7	18.0	.1	.8	18.6	32.1	20.6	9.8
245	7.4	.2	27.2	57.0	2.3	5.9	81.3	20.7	.1	.7	14.8	31.5	20.4	11.8
257	7.0	.0	27.8	57.2	2.4	5.6	83.4	17.8	.0	1.0	19.2	32.7	18.6	10.7
269	7.4	.2	28.0	57.0	1.3	6.1	84.0	20.3	.0	.5	16.4	30.9	20.2	11.7
281	7.4	.1	28.1	56.4	1.6	6.4	84.3	16.8	.2	.7	21.5	34.3	17.5	9.0
293	6.8	.2	28.8	55.3	1.9	7.0	83.0	19.0	.2	.4	18.8	31.0	19.1	11.5
305	6.8	.1	28.3	57.3	1.2	6.3	84.9	15.9	.1	1.0	19.6	35.7	18.7	9.0
317	7.0	.0	27.8	57.8	1.6	5.8	83.4	18.3	.1	.4	19.6	32.0	17.6	12.0
329	6.8	.1	28.3	57.1	1.2	6.5	84.9	15.1	.0	.9	21.0	34.6	16.7	11.7

[a] Material obtained upon treatment with concentrated H_2SO_4.

Original from THE OHIO STATE UNIVERSITY

Table 13.- Change in gas composition with synthesis reaction.

	Experiment life, hours													
	0	24	48	72	96	120	144	168	192	216	240	264	288	312
Gas contraction, percent	52.4	58.2	58.2	57.7	58.6	55.1	60.8	61.9	58.6	55.3	54.7	53.2	53.2	50.3
Synthesis gas														
Composition, volume percent														
CO_2	6.9	6.0	6.3	6.5	6.8	7.2	7.1	6.9	7.2	7.5	7.5	7.4	7.0	6.9
O_2	0.2	0.2	0.2	0.1	0.2	0.2	0.1	0.2	0.2	0.2	0.1	0.1	0.2	0.1
CO	28.3	29.2	28.3	28.1	28.1	27.8	28.4	28.4	28.1	28.0	27.9	28.0	28.4	28.2
H_2	56.4	57.2	57.3	56.2	57.4	56.5	56.0	56.5	56.2	56.1	56.9	57.0	56.8	56.8
"Useful gas"	84.6	85.8	86.0	84.3	84.3	83.4	84.0	84.8	84.3	84.0	83.7	84.0	85.2	84.6
C_nH_{2n+2}	1.8	1.7	1.6	1.7	1.5	1.5	1.6	1.7	1.6	1.6	1.8	1.4	1.4	1.4
N_2	6.4	5.7	6.3	7.4	6.0	6.8	6.8	6.3	6.7	6.6	5.8	6.1	6.2	6.6
H_2:CO ratio	2.16	2.14	2.17	2.04	2.11	2.17	2.09	2.05	2.09	2.10	2.10	2.16	2.10	2.20
Product gas														
Composition, volume percent (Based on 100 mols of product gas)														
CO_2	17.4	15.2	16.0	18.1	17.2	17.1	20.7	20.7	18.7	19.1	18.7	18.2	17.4	16.4
O_2	0.1	0.1	0.2	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.0
C_mH_n	.3	.5	.4	.4	.5	.4	.7	.6	.7	.7	.7	.7	.8	.9
CO	21.2	22.6	22.3	19.9	19.5	20.6	17.7	16.6	18.3	17.8	17.1	18.7	18.6	20.0
H_2	36.5	36.0	38.8	37.9	36.8	36.3	28.0	29.1	32.3	31.6	32.3	33.0	33.2	33.3
C_nH_{2n+2}	13.1	12.7	12.4	12.9	14.5	12.9	19.6	20.8	18.7	18.6	19.7	18.7	19.1	16.9
N_2	11.4	12.9	9.9	10.6	11.4	12.5	13.2	12.1	11.2	12.1	11.4	10.7	10.8	12.5
(Based on 100 mols of synthesis gas)[a/]														
CO_2	8.3	6.4	6.7	7.7	7.1	7.7	8.1	7.9	7.7	8.5	8.5	8.5	8.2	8.1
O_2	0.0	0.0	0.1	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_mH_n	.1	.2	.2	.2	.2	.2	.2	.2	.3	.3	.3	.3	.4	.4
CO	10.2	9.5	9.4	8.4	8.1	9.3	6.9	6.3	7.6	8.0	7.8	8.8	8.7	9.9
H_2	17.4	15.1	16.3	16.0	15.3	16.3	11.0	11.1	13.4	14.1	14.7	15.4	15.5	16.5
C_nH_{2n+2}	6.2	5.3	5.2	5.5	6.0	5.8	7.7	7.9	7.8	8.3	8.9	8.8	8.9	8.4
N_2	5.4	5.3	3.9	4.4	4.7	5.5	5.3	4.7	4.6	5.5	5.1	5.0	5.1	6.4

[a/] Calculated by: (100-gas contraction)(volume-percent of product gas).

TABLE 14. - Results of small scale experiments

Experiment life, hours	Reaction temperature, °C.	Volume of gas used, l.[a]	Gas velocity l./hr.	Contraction, percent	Liquid product distribution					
					Total yield, ml./m.3 synthesis gas				Yield, ml./m.3 synthesis gas	
					H_2O	Diesel oil	Gaso- line	Total oil	H_2O	Total oil
0- 24.............	204.5	88.1	3.7	62.5	13.1	0.6	1.9	2.5	149	28
24- 48.............	206	90.4	3.8	64.6	14.8	1.9	4.1	6.0	164	66
48- 72.............	206	90.0	3.8	64.6	15.1	2.0	5.0	7.0	168	78
				b/(75.1)					b/(195)	b/(91)
72- 96.............	206	89.2	3.7	61.7	14.4	1.8	5.0	6.8	162	76
96-120.............	206.5	87.8	3.7	57.2	13.5	1.8	4.5	6.3	154	72
120-144.............	207	94.2	3.9	61.9	12.4	1.8	3.9	5.7	132	61
144-168.............	210	93.3	3.9	54.3	13.8	1.4	3.8	5.2	148	56
168-192.............	210.5	92.1	3.8	48.0	13.4	1.6	3.4	5.0	146	54
192-216.............	211.5	93.1	3.9	48.7	12.5	1.4	2.9	4.3	134	46
216-240.............	212.5	93.2	3.9	47.7	12.1	1.2	3.5	4.7	130	50
240-264.............	213	94.3	3.9	52.5	11.2	1.1	3.3	4.4	119	47
264-288.............	214	85.0	3.5	45.6	10.7	1.1	2.9	4.0	126	47
288-312.............	215	87.4	3.6	47.8	11.4	1.0	3.5	4.5	131	52
312-336.............	215	85.5	3.6	44.0	10.0	1.0	2.5	3.5	117	41
Total values........	-	1,227.8(?)	-	-	178.4	19.7	50.2	69.9	-	-
Average values......	204-215	-	3.7	53.5 b/(63.3)	-	-	-	-	145 b/(172)	57 b/(67)

a/ Corrected for temperature changes.
b/ Calculated on the basis of 100 percent H_2+CO synthesis gas.

Original from THE OHIO STATE UNIVERSITY

The following properties of the paraffin hydrocarbons, Diesel oil, and gasoline were determined: specific gravity, refractive index, iodine number, distillation curve, and acidity. The acidity of the water fraction also was determined. These results are presented in table 15.

Experimental Procedure; Iron Catalyst

Synthesis Gas Preparation

Production of components, CO and H_2. - A synthesis gas similar in composition to that used in experiment 17, employing a cobalt catalyst, was used in this test. A composition of approximately $2H_2:1CO$ was maintained; thus, its production was very similar to that previously described. A large percentage of useful gas (CO and H_2) was obtained by preparing a water-gas of approximately 37 percent CO (table 16). The hydrogen sulfide was removed, and electrolytic hydrogen was added to produce a $H_2:CO$ ratio of about 1.9:1 at a production level of 100 cubic meters per hour. Using this procedure, the average amount of useful gas in the synthesis gas was 87.2 percent.

Organic sulfur was removed from the mixed gas by passing the gas at 215° to 230° C. over a fixing agent consisting of 500 liters of copper hydroxide, diatomaceous earth, and caustic soda (20 percent copper and 3 percent caustic soda), which had been saved from experiment 17, and then passing it over 500 liters of luxmasse (10 percent copper hydroxide and 10 percent sodium carbonate). The results obtained by this purification treatment are listed in table 17 and show that throughout the whole test the sulfur content of the purified synthesis gas was less than 0.2 gm./100 m.3. The equipment, procedures, and results pertaining to the manufacture and purification of the synthesis gas used in this experiment are very similar to those described experiment 17.

Table 15.- Characterization of product oil

A. Physical characteristics

	d_4^{20}	n_D^{20}	Iodine number (Odor type, pyridine method)	Distillation range, °C.				
				Initial boiling point	10 percent	50 percent	90 percent	95 percent
Total oil	0.7045	1.4018	53.5	35.0	55.0	115.5	265.0	—
Gasoline	.6808	1.3884	58.8	29.0	41.1	78.6	155.0	—
Diesel oil	.7339	1.4174	16.6	96.0	137.8	180.1	232.0	249.0

B. Product acidity

	Total acidity	Inorganic acid	Organic acid
H_2O fraction	2.92	2.75	0.17
Gasoline fraction	0.15	0.03	.12
Diesel oil fraction	.24	.10	.14
Total oil	.20	.02	.18

C. Daily characterization of product

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Gasoline														
d_4^{20}	0.6814	0.6808	0.6841	0.6871	0.6861	0.6839	0.6892	0.6885	0.6826	0.6824	0.6859	0.6845	0.6921	0.6870
n_D^{20}	1.3894	1.3885	-	1.3898	-	1.3914	1.3903	1.3910	1.3914	1.3894	1.3920	1.3906	1.3944	1.3920
Iodine No.	46.5	58.8	75.7	77.3	74.0	78.6	81.5	63.7	87.5	86.3	85.8	89.5	89.1	94.8
Diesel Oil														
d_4^{20}	0.7411	0.7404	0.7339	0.7431	0.7353	0.7422	0.7465	0.7441	0.7421	0.7433	0.7417	0.7465	0.7465	0.7491
n_D^{20}	1.4194	1.4175	1.4174	1.4185	1.4176	1.4191	1.4181	1.4178	1.4189	1.4194	1.4200	1.4208	1.4210	1.4217
Iodine No.	11.3	15.3	16.6	16.9	15.3	17.2	16.8	15.9	18.1	17.3	16.6	17.7	19.4	19.9

Table 16.- Composition of water-gas.

Period over which sample was taken, hr. since start of run	Gas composition, volume-percent						Sulfur content, gm./100 m.^{3}	
	CO_2	O_2	CO	H_2	CH_4	N_2	Total S	Organic S
23-25	8.8	0.0	32.8	50.6	1.2	6.6	18.1	14.8
35-37	6.8	.2	37.3	46.6	1.4	7.7	20.4	17.4
48-50	6.9	.0	37.3	46.0	1.9	7.9	23.8	21.7
58-60	6.9	.1	37.1	48.6	1.1	6.2	23.4	21.7
71-73	8.0	.0	37.8	44.9	2.4	6.9	23.4	20.6
81-83	8.2	.1	36.8	47.8	1.4	5.7	22.7	18.1
95-97	7.9	.1	37.2	47.0	1.4	6.4	--	20.9
105-108	7.3	.1	36.1	49.7	1.1	5.7	22.6	20.5
120-122	8.0	.0	36.7	48.6	0.9	5.8	48.7	22.7
129-132	8.5	.2	36.3	46.5	1.6	5.9	40.8	26.3
144-147	8.2	.1	36.7	48.1	1.4	5.5	47.8	29.5
153-155	8.6	.2	36.1	47.9	1.4	5.7	42.1	26.3
167-170	7.8	.2	37.2	47.2	1.6	6.0	47.9	29.0
177-179	8.1	.1	35.7	47.9	1.7	6.5	36.3	21.4
191-194	7.8	.1	37.3	47.9	1.6	5.3	38.3	23.6
201-203	7.7	.1	37.2	47.4	1.4	6.2	45.8	24.3
215-217	7.5	.1	38.1	47.2	1.4	5.7	42.4	36.1
225-227	7.4	.1	37.7	44.8	1.9	8.1	34.4	26.1
239-242	7.4	.1	37.5	47.4	1.9	5.7	34.7	25.6
249-252	7.4	.1	37.8	47.9	1.6	5.2	41.6	27.4
263-266	8.0	.2	36.5	49.2	1.0	5.1	44.2	27.0
273-276	7.8	.1	37.4	47.1	1.9	5.7	47.6	23.3
287-290	7.6	.2	38.1	48.6	1.1	4.5	46.6	33.0
297-299	7.6	.1	37.5	47.2	1.9	5.7	45.4	23.9
311-314	8.5	.1	36.5	48.6	1.4	4.9	52.8	28.4
321-324	7.7	.1	37.6	47.4	1.9	5.3	48.0	22.6
336-339	7.5	.1	38.3	47.6	1.6	4.9	61.4	31.3
345-347	8.1	.1	37.1	46.7	1.9	6.1	33.9	20.1
360-363	7.7	.1	38.0	48.2	1.4	5.6	67.9	32.5
369-372	6.9	.1	38.5	47.9	1.1	5.4	51.4	25.1
384-386	7.5	.1	38.2	48.0	1.4	4.8	82.3	29.5
393-395	8.0	.1	36.7	47.7	1.4	6.1	43.6	25.2
—	5.8	.1	40.6	46.0	1.1	6.4	33.0	27.7
414-416	6.0	.2	38.9	48.1	1.2	5.7	63.5	22.9
428-430	6.1	.1	39.7	45.3	1.1	7.7	34.5	30.4
438-440	6.6	.1	39.1	45.5	1.4	7.3	69.2	27.6
452-454	6.7	.2	39.0	46.6	1.0	6.5	39.0	27.3
462-464	6.3	.1	38.5	46.6	1.4	7.0	48.9	26.3
476-478	6.9	.1	39.3	46.4	1.3	6.0	58.7	24.1
486-488	7.5	.1	38.1	46.3	1.4	6.6	60.7	23.3
500-502	7.4	.1	38.1	46.8	1.1	6.5	42.0	22.9
510-512	7.4	.1	38.2	46.1	1.3	6.9	40.2	19.7
524-526	7.1	.1	38.8	46.9	1.1	6.0	62.7	27.5
534-536	7.2	.1	38.6	46.3	1.3	6.5	63.3	18.1
549-551	7.8	.1	37.9	46.7	1.1	6.4	41.1	24.9
558-560	7.9	.1	37.8	46.9	1.1	6.2	54.9	18.7
572-575	7.7	.1	38.3	48.0	1.0	4.9	79.0	28.4
582-584	7.6	.1	38.1	46.3	1.4	6.5	28.8	14.3
597-599	6.0	.1	40.2	46.2	1.1	6.4	83.8	25.0
606-608	5.8	.1	42.8	45.2	1.1	6.0	26.3	21.1

TABLE 17. - Removal of organic sulfur from synthesis gas

Period over which gas sample was taken, hour since start of run	Temperature of synthesis gas, °C. Entrance	Temperature of synthesis gas, °C. Exit	Temperature of purifier bed, °C.	Total sulfur content of purified gas, gm./100 m.^{3}
26- 34................	230	205	210-230	0.09
50- 58................	230	205	210-230	.09
74- 82................	230	205	210-230	.13
98-106................	230	205	210-230	.09
122-130................	230	205	210-230	.08
146-154................	230	205	210-230	.10
170-178................	230	205	210-230	.07
194-202................	230	205	210-230	.11
218-225................	230	205	210-230	.11
242-250................	230	205	210-230	.10
270-273[a]...............	230	205	210-230	.10
290-292................	230	205	210-230	.07
314-321................	230	205	210-230	.13
339-345................	230	205	210-230	.19
362-369................	230	205	210-230	.15
386-394................	240	210	215-230	.10
418-425[a]...............	240	210	215-230	.09
430-448................	240	210	215-230	.11
455-473................	240	210	215-230	.07
483-495................	240	210	215-230	.09
503-520................	240	210	215-230	.20
527-544................	240	210	215-230	.14
551-568................	240	210	215-230	.13
575-591................	240	210	215-230	.14
599-617................	240	210	215-230	.11
604-611................	240	210	215-230	.13

[a] Only one value taken; other results are averages of two values.

Catalyst

A mixture of two catalysts of different copper contents was used. These catalysts were made in 35-liter batches, and the batch activities were determined. These batches were blended to form catalyst of average activity, and this mixture was placed in the converter for the test. The determination of the activity of this mixed catalyst is shown in table 18.

TABLE 18. - Determination of catalyst activity

(Catalyst composition = 350 l. of 100Fe:25Cu:2Mn:
20H_3BO_3:4K_2CO_3:125 kieselguhr + 620 l. of 100Fe:
12.5Cu:2Mn:20H_3BO_3:4K_2CO_3:125 kieselguhr; reactor
temperature = 240° C.; synthesis gas = 2H_2:1CO)

Days	Gas flow, l./hr.	Operating time, hours	Contraction, percent	Liquid hydrocarbon products, cc./m.^{3} Diesel oil	Liquid hydrocarbon products, cc./m.^{3} Gasoline	Liquid hydrocarbon products, cc./m.^{3} Total
1.........	3.8	20	29.5	28.8	41.6	70.4
2.........	4.2	23	32.5	36.2	47.5	83.7
3.........	4.3	25	40.9	43.8	45.6	89.4
4.........	3.7	17	40.3	51.4	46.6	98.0

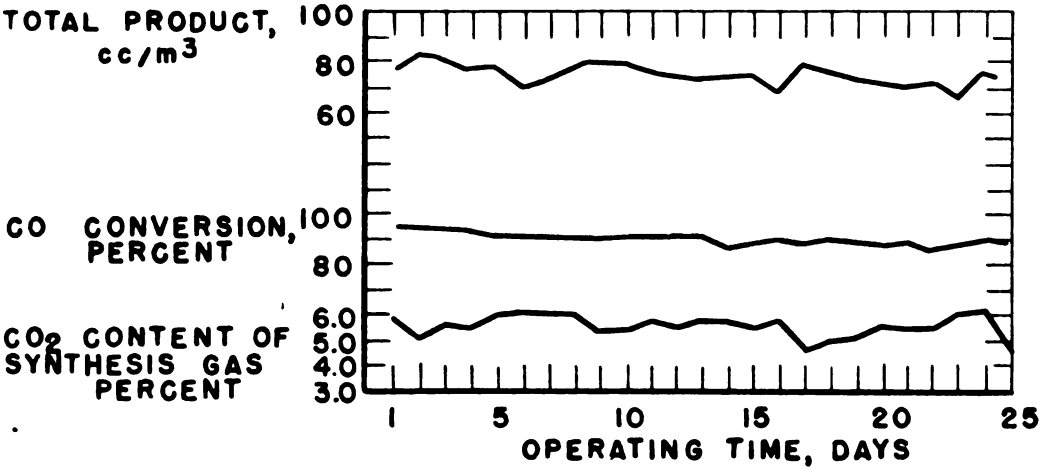


Figure 34. - Operating data for experiment No. 18.

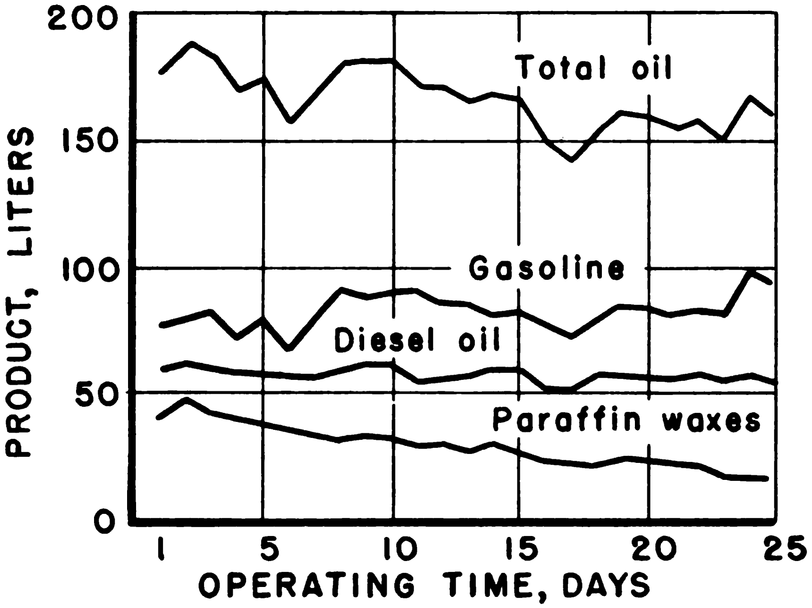


Figure 35. - Yield data for experiment No. 18.

Synthesis Operation

A reaction temperature of 250° C. was anticipated to be the best for iron catalysts, but, by increasing the hydrogen content of the synthesis gas, it was possible to lower the reaction temperature to 235° C., the temperature generally employed in this experiment. A decrease of catalyst activity also was expected with time, and a compensating increase in reaction temperature was therefore anticipated; however, actual operation at these experimental conditions resulted in very little decrease in activity, and it was possible to maintain a constant reaction temperature. To observe the effect of increased temperature, however, 238° C. was maintained for the last 3 days of the test.

Carbon dioxide is formed when iron catalysts are used in the synthesis, and the use of a synthesis gas of the same composition as the usage ratio ($0.5H_2$:CO) results in a very short catalyst life. Using a large excess of hydrogen, however, although it decreases the reaction temperature and increases the catalyst life, is uneconomical. A compromise of these points was found in a synthesis gas ratio of $2H_2$:1CO at a throughput of 100 $m.^3$/hr. (uncorrected for temperature and pressure), which corresponded to a gas space velocity of 100 (catalyst volume = 970 l.).

Plant operation was begun on October 7. After the temperature of the organic-sulfur remover reached the operating point, synthesis gas was passed into the converter, and the converter temperature was gradually increased. By October 8, the hot water temperature had reached 235° C., and 22-percent contraction was achieved, indicating that the reduction of the catalyst had been completed. On the 9th of October, starting at 10 o'clock, data were recorded every 24 hours until 3 o'clock, October 25, when a welded section of a cooling pipe in the converter developed a leak, allowing the hot water to leak into the synthesis chamber and interrupted the run. Repairs were completed the morning of October 27, and the test was resumed; by 1 o'clock on October 28, normal operating conditions were regained. The test continued in a normal manner at a constant temperature of 235° C. with no significant decrease in catalyst activity. During the last 3 days of the experiment, the operating temperature was increased to 238° C. to observe any effect on synthesis operations. The results of this experiment are given in table 19 and figures 34 and 35. The variation in temperature throughout the catalyst bed is shown in table 20, and the change in gas composition as a result of the synthesis reaction is given in table 21. As a reference, the results obtained from a small-scale experiment (flow rate = 4 l./hr.) using the same synthesis gas composition are given in table 22. In all cases, operating time was computed from October 9, and October 25, 26, and 27 were not figured in the total life of the test. The characteristics of the product oil are presented in table 23.

TABLE 19. - Operating conditions and product yields, experiment 18

Operating conditions					Daily product yields								
Time, days	Temp., °C.	Flow of synthesis gas[a]		Contraction, percent	H_2O		Wax, l.	Diesel oil, l.	Gasoline, l.	Liquid + solids		Gasol	
		m.3/day	m.3/hr.		l.	cc./m.3[b]				l.	cc.m.3[b]	m.3	l./m.3[b]
1............	235	2,299	95.6	23.7	36	16	41	60	77	178	77	7.3	3.2
2............	235	2,274	94.7	25.0	44	19	48	62	79	189	83[c] (94.5)	6.5	2.9
3............	235	2,265	94.4	24.3	37	16	42	60	82	184	81	7.0	3.1
4............	235	2,215	92.3	24.4	40	18	40	58	72	170	77	7.0	3.2
5............	235	2,234	93.1	23.5	32	13	37	58	80	175	78	6.5	2.9
6............	235	2,244	93.5	23.9	28	12	36	56	66	158	70	6.5	2.9
7............	235	2,316	96.5	23.2	31	13	34	56	80	170	73	7.0	3.0
8............	235	2,330	97.1	23.6	28	12	32	59	91	182	78	6.0	2.6
9............	235	2,299	95.8	24.4	17	7	33	62	88	183	80	6.5	2.8
10............	235	2,311	96.3	23.6	25	11	32	61	90	183	79	7.0	3.0
11............	235	2,282	95.1	23.0	29	13	29	55	90	174	76	6.5	2.9
12............	235	2,326	96.9	22.9	27	12	30	56	86	172	74	6.5	2.8
13............	235	2,307	96.2	23.1	29	13	27	56	85	168	73	6.5	2.8
14............	235	2,305	96.1	23.0	26	11	30	59	81	170	74	6.0	2.6
15............	235	2,265	94.4	22.8	28	12	27	59	82	168	74	6.5	2.9
16............	235	2,270	94.6	22.2	25	11	23	52	77	152	67	6.0	2.6
17............	235	1,835	87.4	24.6	30	16	22	51	71	144	79	6.0	3.3
18............	235	2,078	86.6	24.3	25	12	22	57	77	156	75	6.5	3.1
19............	235	2,240	93.3	24.6	29	13	24	56	84	164	73	6.0	2.7
20............	235	2,268	94.5	24.5	25	11	24	55	83	162	71	6.0	2.6
21............	235	2,246	93.6	24.4	28	12	22	55	80	157	70	7.0	3.1
22............	235	2,249	93.7	24.5	25	11	21	57	82	160	71	5.5	2.4
23............	238	2,288	95.3	24.9	29	13	17	55	80	152	66	7.0	3.1
24............	238	2,270	94.6	25.8	25	11	16	57	97	170	75	6.5	2.9
25............	238	2,239	93.3	24.5	27	13	16	54	92	162	73	6.0	2.7
Average.......	235		94.2	23.9		13					75 [c] (86)		2.9
Total.....		56,255			725		725	1,426	2,052	4,203		161.8	

[a] Gas-meter values corrected and reduced to standard conditions.
[b] Per cubic meter of inlet gas.
[c] Values within parenthesis have been corrected for the inerts content of the feed gas.

TABLE 20. Temperature variation in synthesis converter.

Time, days	Heating jacket, °C.		Catalyst bed, °C.									Synthesis gas	
	Inlet	Outlet	1	2	3	4	5	6	7	8	9	Flow m.^{3}/hr.	Contraction, percent
0..........	235	235	234	234	235	235	235	239	235	233	234	108.2	27.0
1..........	235	236	234	235	234	235	235	238	235	234	233	100.9	25.3
2..........	235	236	234.5	234.5	235	235	235	237	235	233	233	102.8	26.1
3..........	235	236	234	234	235	234.5	235	238	234.5	232	233	103.1	24.9
4..........	235	236.5	235	235	235	235	235.5	237	235.5	233.5	233.5	102.1	24.1
5..........	235	236	235	235	236	235	236.5	237	235	234	234	106.5	22.9
6..........	235	236	235	235	235	234.5	235	237.5	234.5	233	233	103.6	23.5
7..........	235	236	234.5	234.5	235	233	234.5	237	234.5	233	233	93.9	25.3
8..........	235	236	235	234.5	235	234.5	235	237.5	235	233	233	105.4	23.3
9..........	235	236	235.5	235	235.5	234	235.5	238	235	233.5	233.5	95.0	24.3
10..........	235	236.5	234	234	234	233	234	238	234	232	233	104.4	22.9
11..........	235	236.5	234	234	234	233	234	238	234	232	232	98.8	22.7
12..........	235	237	234.5	234	234	233	234	238	234	232	232.5	108.4	22.9
13..........	235	236.5	234.5	234	234	233	234.5	238	234	232	232.5	102.8	23.4
14..........	235	236	235	234	234	233	235	238	234.5	233	234	103.9	23.7
15..........	235	236	235	235	234	233.5	235	238	234	233.5	233	98.5	22.4
16..........	235	236	235	235	235	233.5	234	238	234.5	232	233.5	100.9	21.5
17..........	235	234	234.5	234	233	231.5	233.5	236	233.5	231.5	231.5	101.4	24.7
18..........	235	234	234.5	234	234	231.5	233.5	233.5	233	232	232	98.9	23.7
19..........	235	234	232.5	231	231.5	229	231	235	234	229.5	230.5	101.7	24.5
20..........	235	234	233.5	233	233	230.5	233.5	236	234	230.5	231	101.4	25.2
21..........	235	234	233	233	233	230	233	235	234	231	231	99.2	23.8
22..........	235	234	232	232	232	229	231	235.5	232	230	230	100.4	24.0
23..........	238	237.5	234	234	234	232	233	238	234	232	231	102.6	25.0
24..........	238	237.5	234	234	234	232	234	239	234	232	232	99.3	26.6
25..........	238	237.5	234	234	234	232	234	238.5	234	232	233	96.3	24.2

Original from THE OHIO STATE UNIVERSITY

Table 21.- Change in gas compositions during synthesis.

	Operating time, days																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Gas contraction, %	23.7	25.0	24.3	24.4	23.5	23.9	23.2	23.5	24.4	23.6	23.0	22.9	23.1	27.0	22.8	22.2	24.6	24.3	24.6	24.5	24.4	24.5	24.9	25.8	24.5
CO conversion, %	93.8	94.4	93.2	92.6	91.3	91.3	90.9	90.9	90.0	90.7	90.7	90.0	89.4	86.4	88.4	89.0	87.9	89.1	88.0	87.0	88.3	85.4	87.3	87.5	87.7
Synthesis gas																									
Composition, vol. %																									
CO_2	5.9	5.1	5.6	5.5	6.0	6.1	6.0	6.0	5.3	5.3	5.7	5.5	5.7	5.7	5.4	5.7	4.5	4.9	5.1	5.5	5.4	5.4	6.0	6.1	4.5
O_2	0.1	0.0	0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.0	0.1
CO	29.4	30.1	29.3	29.7	30.0	29.9	29.6	29.6	29.9	30.1	30.2	30.3	30.1	30.2	31.0	30.1	30.7	30.3	30.0	29.9	30.0	30.1	30.0	30.4	30.8
H_2	57.0	57.8	58.0	57.9	56.2	56.1	56.2	56.7	57.1	56.9	57.1	57.0	56.8	58.0	57.9	57.3	57.0	57.0	57.3	56.9	56.9	57.9	57.0	57.0	57.6
Useful gas	86.4	87.9	87.3	87.6	86.2	86.0	85.8	86.3	87.0	87.0	87.3	87.3	86.9	88.2	88.9	87.4	87.7	87.3	87.3	86.8	86.9	88.0	87.0	87.4	88.4
CH_4	1.4	1.3	1.4	1.5	1.6	1.3	1.5	1.5	1.6	1.9	1.6	1.7	1.7	1.4	1.6	1.5	1.5	1.4	1.6	1.5	1.5	1.2	1.4	1.3	1.3
N_2	6.2	5.7	5.6	5.3	6.2	6.5	6.6	6.1	6.0	5.7	5.3	5.4	5.6	4.6	4.0	5.3	6.2	6.3	5.9	6.2	6.1	5.3	5.5	5.2	5.7
H_2:CO ratio	.48	.52	.52	.51	.48	.45	.49	.50	.57	.52	.49	.48	.49	.50	.48	.48	.54	.50	.53	.53	.51	.59	.56	.57	.53
Product gas																									
Composition, vol. %																									
(Based on 100 mole of product gas)																									
CO_2	26.8	26.5	26.3	26.5	27.5	26.5	26.2	26.4	26.6	26.3	25.7	25.6	26.0	24.8	25.6	25.6	24.8	24.6	24.1	24.7	24.4	24.3	25.5	25.6	24.4
O_2	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
C_mH_n a/	.6	.7	1.0	.7	1.0	1.1	1.1	.9	.9	.9	.9	.9	1.1	.8	1.1	1.1	.9	1.0	1.0	.9	.8	1.3	.7	.9	1.0
CO	2.3	2.3	2.6	2.9	3.4	3.4	3.5	3.5	4.0	3.7	3.7	4.1	4.2	5.3	4.7	4.2	4.9	4.4	4.8	5.1	4.6	5.8	5.0	5.1	5.1
H_2	57.4	57.4	57.6	58.1	56.3	57.3	56.0	56.3	55.3	56.1	56.8	57.1	56.8	58.5	57.9	57.2	56.1	57.1	57.3	56.8	57.3	56.8	56.3	56.4	57.4
CH_4	4.0	4.7	4.3	4.2	4.6	4.1	3.8	5.6	5.4	5.7	5.7	5.5	5.3	4.1	4.7	4.5	5.1	5.3	4.9	5.0	5.7	5.0	5.0	5.0	5.0
N_2	8.8	8.3	7.9	7.6	7.1	7.5	8.1	7.2	7.6	7.2	7.1	6.6	6.5	6.3	5.9	7.0	8.1	7.5	7.8	7.4	7.1	6.7	7.4	6.9	7.0
(Based on 100 mole of synthesis gas) b/																									
CO_2	20.4	19.9	19.9	20.1	21.0	20.2	20.2	20.2	20.1	20.1	19.8	19.7	20.0	19.1	19.8	19.9	18.7	18.6	18.2	18.7	18.4	18.3	19.1	19.0	18.4
O_2	0.1	0.1	0.1	0.0	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
C_mH_n a/	.5	.5	.8	.5	.8	.8	.8	.7	.7	.7	.7	.7	.8	.6	.8	.9	.7	.8	.8	.7	.6	1.0	.5	.7	.8
CO	1.8	1.7	2.0	2.2	2.6	2.6	2.7	2.7	3.0	2.8	2.8	3.2	3.2	4.1	3.6	3.3	3.7	3.3	3.6	3.9	3.5	4.4	3.8	3.8	3.8
H_2	43.8	43.1	43.7	44.0	43.1	43.7	43.0	43.0	41.7	42.8	43.7	44.0	43.7	45.0	44.7	44.5	42.3	43.2	43.2	42.9	43.3	42.8	42.3	41.8	43.3
CH_4	3.0	3.5	3.3	3.1	3.5	3.1	3.8	4.3	4.1	4.4	4.4	4.2	4.1	3.2	3.6	3.7	3.8	4.0	3.7	3.8	4.3	3.8	3.8	3.7	3.8
N_2	6.7	6.2	5.9	5.7	5.4	5.6	6.2	5.4	5.8	5.5	5.5	5.1	5.0	4.8	4.6	5.4	6.1	5.7	5.8	5.4	5.4	5.1	5.5	5.1	5.3

a/ High-molecular-weight hydrocarbons; obtained upon treatment with conc. H_2SO_4.
b/ Calculated by (volume percent of product gas) x (100 - gas contractions).

TABLE 22. - Small-scale test under comparable conditions

Time, days	Temperature, °C.	Synthesis gas: Flow l./hr.	Synthesis gas: Contraction, percent	Liquid products: H_2O cc.	Liquid products: H_2O cc./m.^{3} [a]	Liquid products: Diesel oil, cc.	Liquid products: Light oil, cc.	Liquid products: Total oil cc.	Liquid products: Total oil cc./m.^{3} [a]
1.........	235	92.5	32.9	2.3	25	2.6	4.1	6.7	73
2.........	235	92.4	34.8	2.4	26	3.0	3.7	6.7	73
3.........	235	96.5	33.8	2.6	27	2.8	4.3	7.1	74
4.........	235	90.9	35.0	2.3	26	2.3	4.4	6.7	74
5.........	235	95.0	32.9	2.4	25	2.4	4.0	6.4	67
6.........	235	96.2	34.3	2.4	25	2.7	3.8	6.5	68
7.........	235	90.0	35.2	2.4	27	2.4	3.6	6.0	67
8.........	235	96.8	35.8	2.5	26	2.5	3.5	6.0	62
9.........	235	93.0	36.4	1.1	12	2.9	3.7	6.6	71
10.........	235	91.1	35.9	1.2	13	2.4	3.8	6.2	67
11.........	235	87.6	33.7	1.5	17	1.9	3.8	5.7	65
12.........	235	91.3	34.4	1.0	11	2.2	3.9	6.1	67
13.........	235	94.6	35.8	1.2	13	2.2	3.6	5.8	61
14.........	235	95.4	34.1	2.0	21	2.6	4.2	6.8	71
15.........	235	89.7	33.4	1.0	11	2.3	4.1	6.4	71
16.........	235	92.5	31.5	.9	10	2.2	3.7	5.9	64
17.........	235	94.1	31.6	2.3	24	2.0	3.8	5.8	62
18.........	235	93.2	32.7	2.2	24	1.9	3.4	5.3	57
19.........	235	92.1	31.9	2.4	26	2.0	3.4	5.4	59
20.........	235	90.4	32.9	2.3	26	1.7	3.7	5.4	60
21.........	235	90.6	31.5	1.1	12	2.0	3.9	5.9	65
22.........	235	87.7	38.0	1.1	13	1.9	3.7	5.6	64
23.........	238	90.0	33.0	1.2	13	1.5	3.8	5.3	59
24.........	238	89.8	32.5	1.2	14	1.9	3.7	5.6	62
25.........	238	92.8	31.9	1.1	12	1.4	4.2	5.6	60

[a] Per cubic meter of synthesis gas.

TABLE 23. - Characterization of products

A. Physical characteristics of product oil

Component	Specific gravity, d_4^{20}	Refractive index, n_D^{20}	Iodine number	Total acid number
Gasoline..............	0.6896	1.3980	167	-
Diesel oil............	.7526	1.4270	60	-
Total oil.............	.7301	1.4178	138	0.10

B. Distillation of product oil

Component	Distillation range, °C.						Percent distilled up to-		
	Initial b.p.	10%	50%	80%	95%	End point	150°C.	200°C.	220°C.
Gasoline....	40.0	58.0	92.8	124.5	172.0	206.0	90.0	97.2	-
Diesel oil..	102.0	154.0	205.0	242.5	282.0	-	7.6	46.0	63.4
Total oil...	39.5	68.1	156.0	278.5	-	-	47.2	61.9	66.9

C. Analysis of gasol

Time, days	Composition, percent								
	CO_2	O_2	CO	H_2 a/	C_3+ b/	C_2H_4 c/	C_nH_{2n+2} d/	n	N_2
12................	48.4	0.3	0.7	3.3	29.1	7.5	5.8	3.2	4.9
16................	40.3	1.0	2.0	6.4	21.0	5.7	15.3	1.2	8.3
18................	36.4	1.0	2.0	3.1	26.2	5.3	21.7	1.6	4.3

a/ Determined by adsorption with silver permanganate.
b/ Determined by use of 88 percent H_2SO_4.
c/ Determined by adding 102-percent H_2SO_4 to 0.5-percent Ag_2SO_4.
d/ Determined by bomb method.

Discussion of Results

A study of the product yield data reveals that a maximum oil production (189 l./day; 83 $cm.^3/m.^3$) was reached on the second day. The daily average yield of oil then decreased slowly. Raising the reaction temperature to 238° C. during the last 3 days produced no significant increase in oil yield. These results indicate that a constant operating temperature may be maintained for at least a month when iron catalysts are used under these conditions in the hydrocarbon synthesis. No conclusions may be drawn concerning catalyst life, specific loss of activity, or effect of operating temperature without additional data and longer tests. Because it is known, however, that iron catalysts may be used effectively at temperatures up to 260° C., it may be predicted that, by slowly increasing the operating temperature as needed, a catalyst life long enough to satisfy economic requirements on a commercial scale may be obtained.

In order to increase the catalyst life, a synthesis gas containing about $2H_2$:1CO was used. Accordingly, about 57 percent H_2 remained in the product gas, whereas about 90 percent of the CO was consumed, leaving only 2 to 6 percent of CO in the product gas. No significant increase in oil production may be obtained, therefore, until a synthesis gas richer in CO is used. The usage ratio obtained in this experiment was $0.5H_2$:1CO (see table 21).

Figure 23 shows that although the CO_2 content of the synthesis gas is small it varies inversely with the yield of oil subsequently obtained. This suggests the advisability of removing CO_2 from the synthesis gas before it passes through the reactor.

Digitized by Google Original from THE OHIO STATE UNIVERSITY

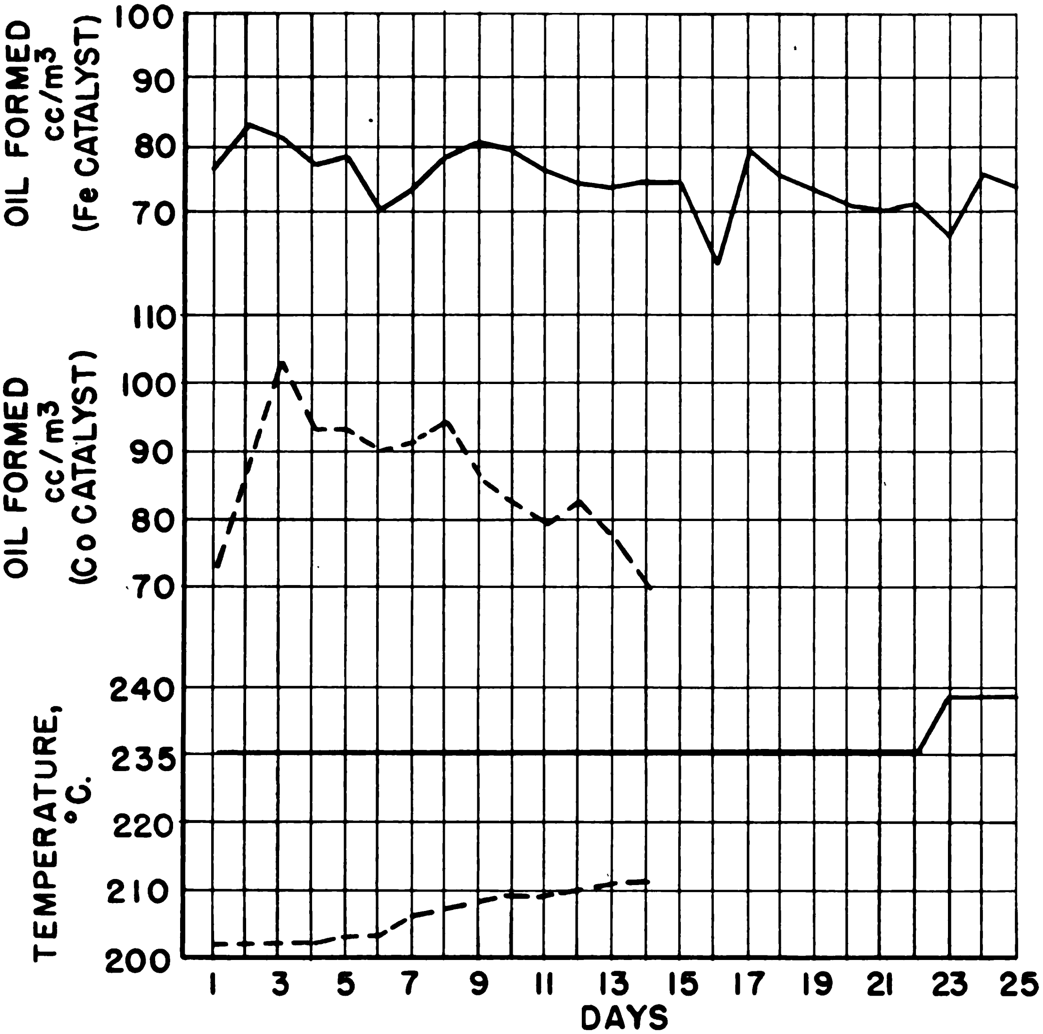


Figure 36. - Co and Fe catalysts; experimental results.

When the production of oil is calculated on the basis of the useful gas (the sum of CO + H_2) in the synthesis gas mixture (excluding CO_2, CH_4, and N_2), a value of 94.5 $cm.^3/m.^3$ of useful gas is obtained, which compares favorably with those results obtained in a laboratory-scale activity test. The average oil production for the entire test is 75 $cm.^3/m.^3$ of inlet gas; on the basis of useful gas, this value becomes 86 $cm.^3/m.^3$. On the basis of a cubic meter of CO + H_2 consumed, the oil production is 180 $cc./m.^3$; this compares favorably with the corresponding value (139 $cm.^3/m.^3$) obtained for cobalt catalysts.

Table 23 shows that 67 percent of the total oil produced distills up to 220° C.; 78 percent of the total oil was obtained as a distillate up to 270° C. It is interesting to note the high degree of unsaturation; that is, the iodine number of the total oil is 138, and that of the light oil stripped from the active carbon adsorbers was 167. Figure 35 indicates a tendency toward lower-molecular-weight products as the synthesis progresses. Comparison of the synthesis oil formed by cobalt catalyst to that formed by iron catalyst shows that the latter has a larger unsaturates content and larger fraction of high-boiling constituents.

Comparison of the results of the two-week test (July 1940) with cobalt catalyst with those obtained from iron catalysts is given in table 24 and plotted in figure 36.

TABLE 24. - Comparison of results obtained during synthesis with cobalt and with iron catalysts

	Cobalt	Iron
Operating time, days	14	25
Initial temperature, °C.	202	235
Final temperature, °C.	211	238
Total amount of synthesis gas used, $m.^3$	26,729	56,255
Total oil formed:		
Liters	2,288	4,203
$cc./m.^3$ of synthesis gas	86	75
$cc./m.^3$ of useful gas	102	86
$cc./m.^3$ of H_2+CO reacted	139	180

When the iron catalyst was used in laboratory-scale tests, no formation of water was noticed; in a large-scale test such as this, however, water was detected in the product. Moreover, in this test, possibly due to the low reaction temperature, gasol formation was small, averaging 3 $l./m.^3$ of synthesis gas (table 19). The composition of the gasol fraction is given in table 23-B.

Thus, there seems to be justification for using iron catalysts industrially, but because a synthesis gas is used that differs in composition from the theoretical, the exit gas has the following average percentage composition: $CO_2 = 25.7$, $O_2 = 0.1$, $C_mH_n = 1.0$, $CO = 4.1$, $H_2 = 56.7$, $CH_4 = 4.9$, and $N_2 = 7.5$. A method of recirculating this tail gas would greatly improve

Digitized by Google Original from THE OHIO STATE UNIVERSITY

the efficiency. For this purpose, a simple flow sheet is proposed in figure 37, in which, first, the CO_2 is removed from the waste gas, and, second, the hydrogen is recirculated after passing through the condenser. The CO_2 removed from the tail gas could be reacted with the methane in coal gas in a special CO generator; the reduction of CO_2 by means of coke is not economically sound because of the high temperature (combustion with O_2) required. The CO formed by reaction with coal gas is then mixed with the recirculating H_2 to form additional synthesis gas. By this procedure with iron catalyst, 7.5 l. of synthesis gasoline and 8.4 kg. of coke could be produced from 50 kg. of coal.

CALCULATION OF HEAT TRANSFER DATA

The types of calculations employed in determining the heat-transfer characteristics of the various converters studied are exemplified by those shown below for a 24-hour period (July 22-July 23) during operation of the 100-m.³/hr. water-cooled converter using a cobalt catalyst.

Based on the average composition of the synthesis gas (table 6) as well as the average extent of reaction and analysis of the product gases (table 9) for that 24-hour period, a value for the heat of reaction of 7,854 kcal./mol was obtained. Reduced to one cubic meter of synthesis gas, this value becomes 350 kcal., and, at the throughput of 1,865 m.³ during this time, the heat generated in the converter was calculated to be

$$\frac{350 \times 1{,}865}{24} = 27{,}200 \text{ kcal./hr.}$$

From table 10, the average temperature differential between cooling medium and catalyst bed was observed to be 4.8° C.; the cooling surface available in this converter was 139.05 m.². From these data, the over-all coefficient of heat transfer could be obtained; thus

$$U = \frac{27{,}200}{4.8 \times 139.05} = 40.75 \ (\text{kcal.})(\text{m.}^2)^{-1}(\text{hr.})^{-1}(\ \text{C.})^{-1}.$$

In these calculations, the heat of reaction was divided by the average difference in temperature, a situation not at all representative of actual conditions in the converter, as the reaction does not proceed in a uniform manner throughout the bed but is concentrated in that portion of the catalyst nearest the gas inlet. Actual calculations of such point-to-point conditions, however, would prove extremely complicated.

Where heat is transferred, as it is in this case, through a gas film, an intervening metal wall, and a liquid film, by far the greatest resistance to the heat flow is offered by the gas film. Thus, the over-all coefficient of heat transfer obtained above may be assumed to approximate that of the heat-transfer coefficient existing across the gas film. In designing the 100-m.³/hr. convertor, some estimates were made of the gas film coefficient. How well these estimates were substantiated by subsequent experimental evidence will be discussed below.

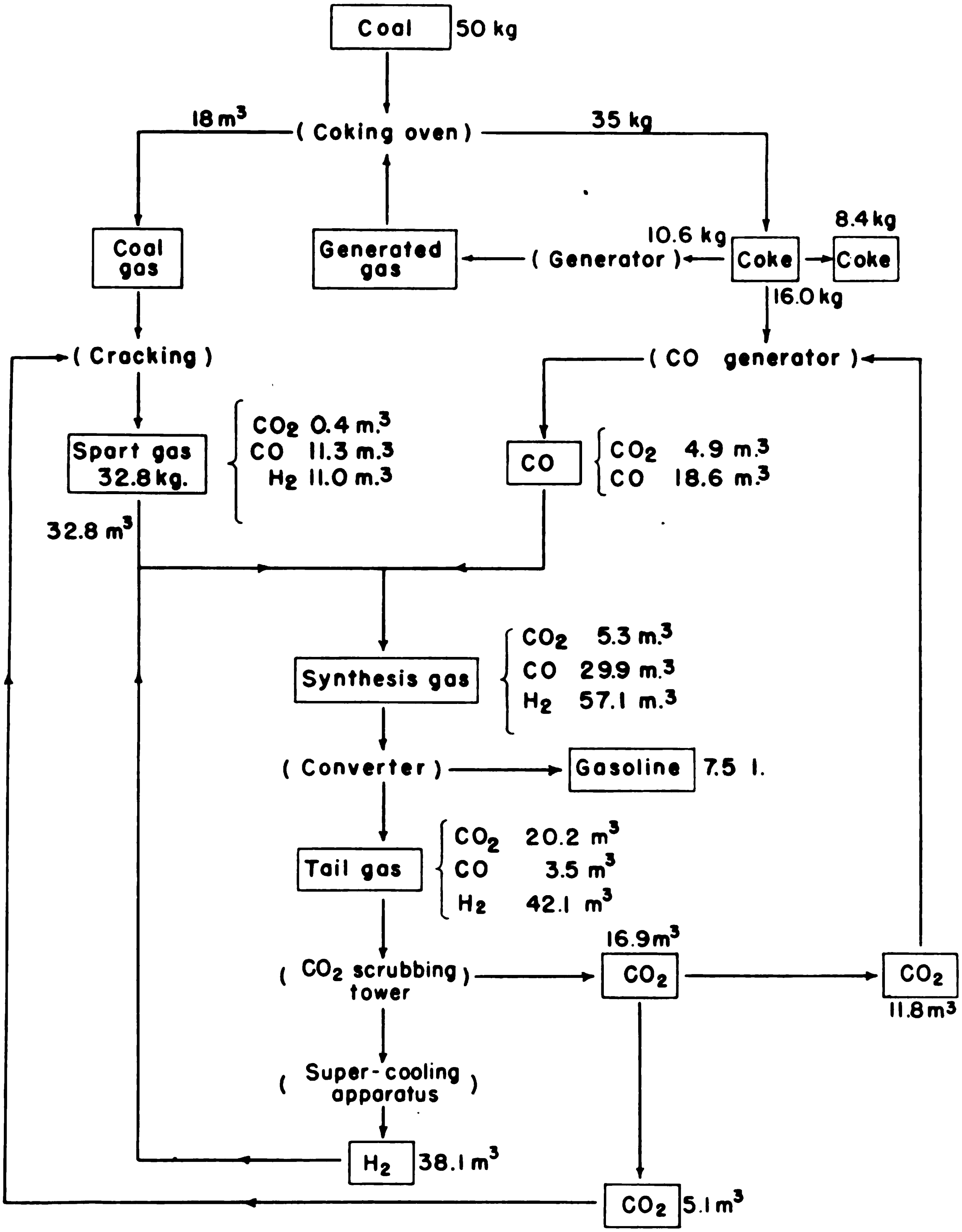


Figure 37. - Proposed flow diagram for recirculating tail gas.

Although the 100-m.^{3}/hr. converter utilizes the cooling medium inside tubes while the reaction gases flow around the outside of the tubes, estimates of the film coefficients were made on the basis of an inner-catalyst converter (gases inside tubes; coolant outside tubes) containing four 25-mm. I.D. tubes, such as the converter shown in figure 2. This was done to simplify the necessary calculations. Assuming a constant hourly flow of gases through the tubes as 100 liters at 200° C., the gas velocity within the catalyst tubes is given by

$$\frac{(100)\ (1,000)(4)(473)}{(2.5)^2(\pi)(3,600)(4)(273)} = 2.45 \text{ cm./sec.}$$

Of course, the volume of the gases is reduced in their passage through the tubes because of the reactions occurring, but this effect has been disregarded. The resulting velocity (2.45 cm./sec.) is much lower than that usually used in industry and gives rise to a Reynolds number of

$$\frac{(2.5)(0.316)(2.45)}{(1,000)(2,351)(10)^{-7}} = 8.3$$

which suggests that a reasonable estimate might be made by assuming that heat is transferred through the gas only by convection in an empty tube. The Grashof and Prandtl numbers were calculated as

$$N_{Gr} = \frac{L^3 \rho^2 \beta g \Delta t}{\mu^2} = 212.0$$

and

$$N_{Pr} = \frac{c\mu}{k} = 0.436$$

by using the following values:

L = inside diameter of catalyst tube = 25 cm.

ρ = density of the gas = 0.000316 gm./cm.^{3}

β = coefficient of expansion of the gas = $\frac{1}{273}$ °C.$^{-1}$

g = acceleration due to gravity = 980 cm./sec.^{2}

Δt = temperature difference between gases and cooling surface = 2°C.

μ = gas viscosity = 2,351 x 10^{-7} poise

c = specific heat at constant pressure = 0.578 cal./gm.

k = specific thermal conductivity = $\frac{0.112}{360}\ \frac{\text{cal.}}{\text{sec. °C.}}$

Thus,

$$\log (N_{Gr})(N_{Pr}) = 1.9626$$

and, from the diagram on page 156 of Uchida's book,

$$\log \frac{hd}{k} = 0.34,$$

yielding the film coefficient

$$h = (1.22)\ \frac{(2.19)(0.112)}{(2.5)} = 11.88\ (\text{kcal})(\text{m.}^2)^{-1}(\text{hr.})^{-1}(^\circ\text{C.})^{-1}$$

where 1.22 is the coefficient for erect pipes.

It is evident, therefore, that the over-all heat-transfer coefficient (U = 40.75) is much greater than the gas film coefficient, h, calculated for heat transfer only by free convection. It is believed that this difference in coefficients is a result of (1) the effect of turbulence caused by the flow of gases around the catalyst granules in the packed tubes and (2) existence of a partial liquid film inside the catalyst tube resulting from formation of liquid products in the synthesis.

Application of an equation developed by A. P. Colburn for calculating the gas film coefficient in tubes for turbulent flow at the critical velocity resulted in a value even smaller:

$$h = 8\ aC_p Z^{0.2} G^{0.83} = 4.10\ (\text{kcal.})(\text{m.}^2)^{-1}(\text{hr.})^{-1}(^\circ\text{C.})^{-1}$$

where

h = gas film coefficient of heat transfer

a = constant depending on size of pipe

C_p = specific heat of gas at constant pressure = 0.578 $(\text{kcal.})(\text{kg.})^{-1}(^\circ\text{C.})^{-1}$

Z = viscosity of gas = 2,351 x 10^{-5} centipoise

G = mass velocity of gas = 0.000316 x 2.45 $(\text{gm.})(\text{cm.})^{-2}(\text{sec.})^{-1}$

It is obvious that Colburn's equation does not apply in this case and demonstrates the importance of the state of gas flow in the selection of a suitable method of film coefficient calculation.

SUMMARY

1. Using a cobalt catalyst in a water-cooled converter (designed for synthesis gas throughput of 100 m.^3/hr.), a 2-week run was carried out successfully.

2. Over a reaction temperature range of 200° to 215° C. and at an average gas throughput of 79.6 m. /hr., the following average yields were obtained at an average apparent contraction of 56.2 percent: 168 ml. of water, 86 ml. of primary liquid products (oil), and 7 liters of gasol per cubic meter of synthesis gas. Correcting these results for the 15.5 percent of inerts contained in the synthesis gas produced an actual contraction of 66.5 percent and increased the yield values to 199 ml. of water, 102 ml. of oil, and 8 liters of gasol per cubic meter of pure $2H_2:1CO$ gas.

3. These results suggest that commercial synthesis of gasoline and hydrocarbon oils in a water-cooled converter may be economically feasible.

4. Using the 100 $m.^3$/hr. converter and an iron catalyst, a continuous run of one month was conducted.

5. No significant decrease of catalyst activity was noted over a period of one month using a synthesis gas of $CO:H_2 = 1:2$.

6. The average amount of oil formed was 75 cc./$m.^3$ of synthesis gas (on basis of useful gas, 86 cc./$m.^3$); this compares favorably with the corresponding yields using cobalt catalyst.

7. The product oil rich in unsaturated compounds.

8. If iron catalyst is used with a hydrogen-rich feed gas, the H_2 in the exit gas must be recirculated for maximum efficiency.

9. Comparison of the results of the synthesis of hydrocarbons in various converters having different ratios of cooling surface to catalyst volume (A/V) it was possible to determine the optimum A/V for use in future designs. The results are compared in table 25. It is evident from these data that locating the catalyst outside the cooling tubes is preferable, as less cooling surface is thus required. (The number of plus signs in the right-hand column of table 25 indicates the merit of the furnace.) The table shows that the best arrangement tested was that of an outer-catalyst converter where a cooling surface of 1.32 $cm.^2$ was present for every cubic centimeter of catalyst.

TABLE 25. - Comparison of cooling surface areas of various converter designs

Type of converter	Throughput, $m.^3$/hr.	Coolant	Tube I.D., mm.	Center-to-center spacing of tubes, mm.	A/V	Measure of merit, (-)<(0)<(+)
Inner-catalyst....	(100 l.)	Oil	55	-	0.728	-
Do.	(100 l.)	do.	35.7	-	1.120	0
Do.	(100 l.)	do.	25.0	-	1.600	+++
Outer-catalyst....	3	Water	-	48 x 42	.963	+
Do.	10	do.	-	45 x 39	1.261	++
Do.	6	do.	-	42.5 x 36.2	1.345	+++
Do.	100	do.	-	42.5 x 36.8	1.322	+++